WSolids1 — Solid State NMR Simulations

User Manual

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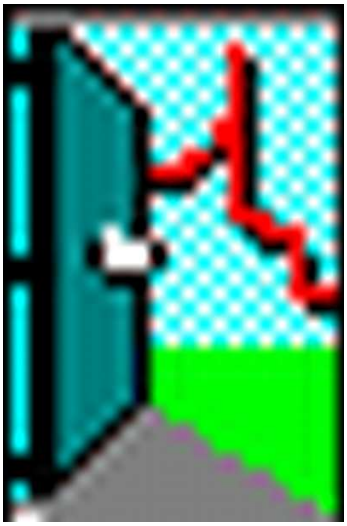
1 Getting Started



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1.1 Introduction

1.1.1 Purpose of the Program

WSolids1 is a program for the visualization and analysis of processed one-dimensional solid-state NMR data. It is a simulation package initially developed at the Department of Chemistry (p. 3), Dalhousie University (p. 4), Halifax, Canada, in order to deal with the multitude of interactions observed in NMR spectra of static or spinning solid samples. The initial versions have been written in C++ using Borland C++ 4.5. However, in spring 2008 the developments, or the lack of such, at Borland made me change my programming tools to Microsoft Visual C++ 2008 Express Edition. Not that this development environment has everything that I would need to work efficiently, but it is for free (it's like they give you a free car without a seat for the driver—it's workable but a bit bumpy at times). WSolids1 succeeds its earlier FORTRAN version, Solids.

Although there are several "general purpose" programs or libraries available to calculate many interactions and for many different experiments, there is still room for programs with specially designed specific calculation models. The main reason is efficiency. A routine designed for one particular purpose will always be more efficient than a general purpose routine! Progress in computing power continually decreases the gap. However, calculation of a static powder pattern of an isolated spin pair using a general purpose program still requires several hours as compared to the few seconds using the less general implementation in WSolids (the "several hours" was written in the mid/end nineties; in 2015, this difference has dwindled). The advantage for the user is convenience rather than power; not every user has the knowledge to feel comfortable with, for example, Simpson (`http://www.bionmr.chem.au.dk/bionmr/software/simpson.php`).

Figure 1.1: The Department of Chemistry at Dalhousie University, Halifax, Canada

Figure 1.2: The logo of Dalhousie University, Halifax, Canada

1.1.2 Features

This section lists some of the features of WSolids1, the knowledge of which should enable the user to work more efficiently with WSolids1:

- WSolids1 uses the Multiple Document Interface (p. 12) (MDI) specification. The user should familiarize himself with this specification. Often, the vendors of NMR spectrometers provide some means of analyzing or simulating experimental spectra, but often a mere simulation – to answer a question like "how would this look like?" – without an experimental spectrum is not possible. MDI as implemented in WSolids1 allows to calculate spectra for different external magnetic fields, different derivative modes, or different experimental conditions simultaneously, using the same spin system parameters. This could help to answer a question like "does it make sense to go to a higher field?"
- Spin systems and spectra are allocated dynamically. One may have as many spectra and spin systems as the memory resources of the computer allow. In each case, the spectrum and spin system parameters are filled with sensible default values. This should allow for easy familiarization.
- WSolids1 has no build-in features to support iterative fitting. In order to make the refinement of a calculated spectrum less painful, a so-called Cycle (p. 38) feature was implemented. Depending on the context and the selected Cycle options, pressing the Enter key will perform specific actions such as requesting spectrometer settings, requesting spin system parameters, requesting convolution parameters, performing a calculation, or switching to the next spectrum window.
- For several menu commands, accelerator keys (p. 14) have been defined (for example, pressing **C** starts a calculation). Also, holding down the **ALT** key and pressing any character key activates the corresponding menu item, edit control, list box, button, etc. for which the corresponding character is underlined.

Some of the description of features has already been formulated in the early nineties. Nowadays, with gigantic office software suites the user is certainly more accustomed to multiple documents etc., but I guess it doesn't hurt to keep this description. Also, the look of WSolids1 is now archaic, but remember: I am a one-man company and not making any money out of this software that I develop and maintain in the evening hours.

1.1.3 License

This program package can be used without any fee. However, if you find this program useful and publish results obtained by using WSolids1, we would appreciate a citation or acknowledgment of this program similar to:

WSolids1 ver. 1.21.3, K. Eichele, Universität Tübingen, 2015.

Before reading on, you may also want to have a look at our credits statement (p. 101), trademark acknowledgment (p. 102), copyright message (p. 102), and obligatory disclaimer (p. 104).

1.1.4 Trouble?

Although WSolids1 has been tested and used both in-house and by others, it is always possible that errors exist. Some errors may become apparent after detailed use on the wide variety of chemical systems. It is the responsibility of the user to determine the correctness of the results. If errors are noticed, please notify us of your problems, and the prescribed or suggested corrections, so that others may benefit from the improved code. Also, suggestions for improvements are welcome.

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1.2 Overview

The overview provided here is aimed at giving an outline of the steps required to achieve a particular task. Following a question in the left column, links to the relevant topics are provided. After catching up on any specific topic, use the **Back** feature of your reader to return to this screen.

How do I start?	① Create a new spectrum window (p. 17) ② Read an experimental spectrum (p. 18) ③ Create a new spin system (p. 35) ④ Define convolution parameters (p. 32) ⑤ Calculate (p. 38) ⑥ Repeat as required (p. 38), using the cycle feature ⑦ Save the results (p. 22)
How do I work efficiently?	Use keyboard accelerators (p. 14) Use the cycle feature (p. 38)

1.3 Revision History

This page describes changes made to the WSolids1 program versus previous versions and provides a summary of new features.

1.3.1 Version 1.21.3 (30.07.2015)

- new feature: added a dialog Settings (p. 40) to change some program settings, either temporarily or permanently
- new feature: added the direct calculation of spinning sidebands; this allows the simulation of MAS spectra in the MAS: Chemical Shift Anisotropy (HB) (p. 62) and MAS: Dipolar-Chemical Shift (A2, AX) (p. 64) models at slower spinning speeds, where the number of spinning sidebands exceeds the limits of the Herzfeld-Berger tables. This functionality was also added to the VAS: Dipolar-Chemical Shift (A2, AX) (p. 76) model, that used to calculate spectra in the high-spinning speed limit only
- new feature: the title of the spectrum window can be longer than 30 characters in the Display Options (p. 39) dialog
- new feature: the spectrum window remembers the file type if a spectrum has been read previously and sets this as default extension (for the current session)
- new feature: added export (p. 22) of spectra in ASCII and JCAMP-DX format
- new feature: the location of the INI file (p. 97) has changed: in the pograms directory for the portable version, or in the user's documents directory
- new feature: Table of Nuclear Properties (p. 42) lists Larmor frequency and frequency of the chemical shift reference compound, Periodic System of Elements (p. 44) lists the frequency of the chemical shift reference compound; the sign of Larmor frequency and reference frequency reflect the sign of γ; the form field for entering B0 is now a combo box that allows entering a field or selecting one from a list
- new feature: added support for PDF-XChange Editor (by Tracker Software Products, Ltd., `http://www.tracker-software.com`) as PDF viewer to display context sensitive help (p. 47)
- new feature and bug fix: the HR: Spin-1/2 Coupled to Quadrupolar Nucleus (Relaxation) (p. 80) model got a few options added to enable some calculations of solid state NMR spectra; the calculations erroneously had a factor of 2, so that the real T_1 should be half of that reported

1.3.2 Version 1.20.22 (06.03.2014)

- new feature: added spin system MAS: Dipolar-Chemical Shift (A2, AX) (p. 64)
- new feature: new document (p. 17) menu item

1.3.3 Version 1.20.21 (15.03.2013)

- Basically a face lift:
- new feature: proportional scroll bars with additional accelerator keys (Pos1, End, Page Up, Page Down)
- new feature: added mouse zooming and scrolling
- new feature: the report (p. 24) feature has added support for SVG display in Internet Explorer 9

1.3.4 Version 1.20.18 (31.01.2012)

- new feature: after reading or writing a WSolids document, the main window title shows the name of the document
- new feature: the report (p. 24) includes a graphical representation of spectra
- bug fix: for reading from or writing to XML documents the MAS: Spin-1/2 – Spin-S (Diag.) (p. 67) spin system, deal properly with the relative intensity and the speedy flag

1.3.5 Version 1.20.15 (25.02.2011)

- new feature: allow to read (p. 22) or write (p. 23) spin system only
- new feature: information on creating reports (p. 24) from the WSolids1 XML document, using XSL transformation files and style sheets
- new feature: added a tool to reference (p. 45) spectra
- new feature: added a checkbox to the Spectrum Default Parameter (p. 28) box to re-initialize (p. 29) the parameters of the calculated spectrum
- new feature: there is an ini file parameter OutFile (p. 98) to set the spectrum output default format
- new feature: there is an ini file parameter NT (p. 98) to set the number of triangular intersections of the POWDER space tiling and interpolation algorithm
- new feature: there is an ini file parameter Digits (p. 99) to fine tune the number of digits displayed in dialog boxes for floating point numbers
- new feature: added support for other PDF viewers to display context sensitive help (p. 47): added handling of PDF XChange Viewer (by Tracker Software Products, Ltd., `http://www.tracker-software.com`), **currently my prefered PDF viewer**, and Sumatra PDF Viewer (`http://blog.kowalczyk.info/software/sumatrapdf`), also deal with the new Adobe Reader X (p. 47).
- new feature: added a new spin system that actually is a high resolution, solution, system: HR: Spin-1/2 Coupled to Quadrupolar Nucleus (Relaxation) (p. 80), **this calculation has not been verified yet, use at your own risk**
- new feature: added a new spin system consisting of three spins: Static: Three-Spin System (AMX) (p. 61), **this calculation has not been verified yet, use at your own risk**
- new feature: for the MAS: Spin-1/2 – Spin-S (Diag.) (p. 67) spin system implemented a general approach that sets up the Hamiltonian on the fly, there are no restrictions on the spin anymore
- bug fix: setting site dependent convolution parameters when reading XML documents
- bug fix: reading JCAMP-DX (p. 21) files

1.3.6 Version 1.20.4 (15.06.2010)

- Fixed reading spin-1/2 nuclei in MAS Spin-1/2 – Spin-S (Stick) (p. 70) WSolids documents

1.3.7 Version 1.20.3 (04.06.2010)

- Fixed a bug in model MAS Spin-1/2 – Spin-S (Stick) (p. 70) when reading WSolids documents

1.3.8 Version 1.20.2 (25.05.2010)

- added saving of all data in XML format as WSolids document

1.3.9 Version 1.19.15 (02.10.2009)

- fixed a bug in adding spectra from several sites
- fixed a bug in calculating MAS spectra of spin-1/2 coupled to quadrupolar nucleus ("stick" approach)

1.3.10 Version 1.19.12 (20.05.2009)

- The Tools—Scale spectrum (p. 44) dialog now presents a scaling suggestion.

1.3.11 Version 1.19.10 (06.01.2009)

- Can read a second spectrum (p. 22) into the memory assigned as calculated spectrum, for dual display with the experimental spectrum

1.3.12 Version 1.19.2 (21.08.2008)

- This is the first 32 bit release. Internally, Wsolids1 underwent some serious changes that will not be apparent to the user.
- Added reading of TopSpin/XWinNMR (p. 19), JCAMP-DX (p. 21), and Simpson (p. 22) files, removed handling of Antiope, NMRLAB and CC2X files.
- In addition to WinNMR format, spectra can also be saved as TopSpin or Solids files
- Incorporated the IUPAC Recommendations 2001 for the NMR properties of NMR active isotopes, the new Q values from Pyykkö; fixed spin of Nd-145 and U-235 and added U-233
- MAS: Spin-1/2 Spin-S (Diag.) (p. 67): added handling of general spin-5/2 case (any-chi, any-eta, any-orientation) and made some modifications to the spin-3/2 part also

1.3.13 Version 1.17.30 (23.05.2001)

- Included new Herzfeld-Berger tables that are more accurate at higher values of μ. The tables were calculated using a home-made dedicated program on a Pentium 400 MHz PC and required almost a week of computer time.

1.3.14 Version 1.17.28 (27.09.2000)

- Changed the use of the Relative intensity (p. 88) parameter; it is now introduced after the calculation for that specific site has been carried out; sites using different calculational models should now have relative areas corresponding to their relative intensities. This also fixed bugs for some of the models where the relative intensity was not handled properly.
- Modified the model Static: Quadrupolar Nucleus (p. 58) to allow a homonuclear A2 spin system (it is up to the user to decide if the result makes sense). A division by zero for not initialized spectrometer frequency gets caught now.
- Modified the POWDER routine by Alderman (previously, the interpolation did not cover the half sphere completely).

1.3.15 Version 1.17.22 (17.03.1999)

- Fixed a bug related to the relative intensities of several sites when using the model MAS: Quadrupolar nucleus (p. 65).
- Made changes to the POWDER subroutine to deal with single-line lineshapes better (previously, no intensity got added).

1.3.16 Version 1.17.21 (09.10.1998)

- Changed the meaning of SF (p. 29) (spectrometer frequency): this parameter corresponds now to the frequency of the chemical shift standard.
- Fixed a bug in model MAS Spin-1/2 – Spin-S (Stick) (p. 70): the factor dealing with reference SF and different Larmor frequencies worked in the opposite sense of the intended direction.
- Added Tools/Add constant (p. 45) to allow for a very simple baseline correction.
- Added Tools/Absolute value (p. 45) to generate the absolute value representation.
- Added Tools/Reverse spectrum (p. 45) to reverse the sense of a spectrum.
- Problems with the cycle feature (p. 38) got probably fixed now.
- Introduced an option in the convolution of spectra to switch off the use of a threshold value (p. 31).
- Different sites calculated with the model MAS: Chemical Shift Anisotropy (HB) (p. 62) should have the proper relative intensities now.
- Added functions to read experimental spectra in Chemagnetics SpinSight (p. 20) format.
- Added functions to read WinNMR ASCII (p. 20) spectra directly, without the need to convert them into SOLIDS format.

1.3.17 Version 1.17

- Added a new calculation model: MAS: Quadrupolar nucleus (p. 65).
- Fixed a memory problem (bug) in model MAS Spin-1/2 – Spin-S (Stick) (p. 70) and modified processing.
- Changed the handling of spectrum files. WSolids1 now uses the NMRFILES dynamic link library developed for WSolids2, which allows for a greater variety of file formats.
- Fixed another error in model MAS: Spin-1/2 Spin-S (Diag.) (p. 67); cup = 1 for sth = 0
- Modified processing in model MAS: Spin-1/2 Spin-S (Shape) (p. 74)
- Added Tools/Scale spectrum... (p. 44) to allow scaling of spectrum
- Modified enabling/disabling of controls in convolution parameter box; changed layout of dialog box

1.3.18 Version 1.16

- Fixed cycle feature. (Actually, not really; fixed one problem, created a new one)
- Fixed MDI accelerators.
- Processing modified for the following dialog boxes: default parameters, convolution parameters, model selection, static chemical shift anisotropy, static dipolar chemical shift (A2, AX), static dipolar chemical shift (AB), static quadrupolar nucleus, MAS chemical shift anisotropy (HB), MAS spin-1/2 – spin-S (Diag.), About, Open file, Save file, Edit sites

- Fixed errors in model Static: Dipolar−chemical shift (A2, AX) (p. 52) and VAS: Dipolar-chemical shift (A2, AX) (p. 76): for A2 system, J is neglected now.
- Fixed two errors in model MAS: Spin-1/2 Spin-S (Diag.) (p. 67): sign error in sbsf term; cet = 1 for cth = 1.
- Fixed update of BF1 in AQS file.
- Fixed file handling functions to use WinAPI exclusively (should allow to create and read more files).

1.4 Multiple Document Interface, MDI

This topic provides some information about the Multiple Document Interface in general and its implementation in WSolids1. Managing multiple documents is one of the key issues.

1.4.1 The Multiple Document Interface

The multiple document interface (MDI) has been designed for applications that need to simultaneously manage:

- more than one data set
- more than one view of a data set

In MDI, there are two fundamentally different type of windows:

- The main window of an MDI application is called a "**frame**" window. Frame windows usually have:
  - a title bar
  - a menu, a system menu
  - a sizing border
  - Minimize/Maximize buttons

  The non client area of the frame window surrounds a portion of something called the application "**workspace**". The workspace can be larger than the frame window's client area, because a user can use scroll bars to scroll different portions of the workspace into view.
- An MDI application's workspace can contain zero or more child windows, which are referred to as "**documents**", "document windows", or "MDI children." In the case of WSolids1, a document window usually corresponds to a window with dual display of an experimental and a calculated spectrum. We shall call such a document window a **spectrum window**.
  In general, document windows have:
  - a title bar
  - a sizing border
  - a system menu bitmap
  - Minimize/Maximize buttons
  - scroll bars

Because document windows always have Minimize and Maximize buttons, they can be minimized and maximized. When minimized, they are represented as icons and displayed in the workspace of the frame window. When maximized, document windows are sized to fill the entire workspace of the frame window, not the entire Windows desktop. The title bar of a maximized document window disappears and its caption text is appended to the caption text in the frame window's title bar. In addition, the system menu bitmap of the document window becomes the first item in the menu bar of the frame window, and the button to restore the document window to normal size is positioned at the far right of the frame window's menu bar.

1.4.2 Menu Management

The frame window's menu bar has a popup menu bar item called Window near the right end of the menu (just left of the Help item). The Window popup menu contains items related to the arrangement of document windows within the workspace. These options include tiling and cascading of windows and arranging icons at the bottom of the workspace.

1.4.3 Keyboard Interface

The Windows MDI has its own keyboard interface that augments the keyboard interface for non-MDI applications. The MDI key sequences allow users to easily navigate between and manipulate document windows within an MDI application just as they can navigate between and manipulate applications on the Windows desktop (see also the section on keyboard accelerators (p. 14) in WSolids1).

- CTRL + F4 closes the currently active document window. (ALT + F4 closes an application's main window.)
- CTRL + F6 (or CTRL + TAB) switches among document windows in the MDI application's workspace (ALT + TAB switches among applications on the Windows desktop.)
- ALT + HYPHEN invokes the system menu of the active document window (ALT + SPACEBAR invokes the system menu of the active application's main window.)

1.5 Keyboard Accelerators

ALT + F4	closes an application's main window
ALT + HYPHEN	invokes the system menu of the active document window
ALT + SPACEBAR	invokes the system menu of the active application's main window
ALT + TAB	switches among applications on the Windows desktop
CTRL + F4	closes the currently active document window
CTRL + F6	switches among document windows in the MDI application's workspace
CTRL + TAB	switches among document windows in the MDI application's workspace
ENTER	perform the next step of the cycle feature
C	Calculate
E	Edit sites
N	New Site
CTRL-→	zoom-in spectrum window horizontally
CTRL-←	zoom-out spectrum window horizontally
CTRL-↑	zoom-in spectrum window vertically
CTRL-↓	zoom-out spectrum window vertically
→	scroll spectrum window horizontally to display lower frequencies
←	scroll spectrum window horizontally to display higher frequencies
↑	scroll spectrum window vertically to display higher intensities
Page Up	scroll spectrum window vertically in greater steps to display higher intensities
Pos1	scroll spectrum window vertically to the top to display highest intensities
↓	scroll spectrum window vertically to display lower intensities
Page Down	scroll spectrum window vertically in greater steps to display lower intensities
End	scroll spectrum window vertically to the bottom to display lowest intensities

2 Menus

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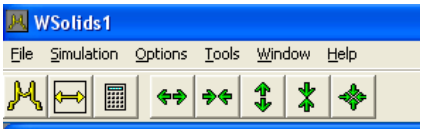
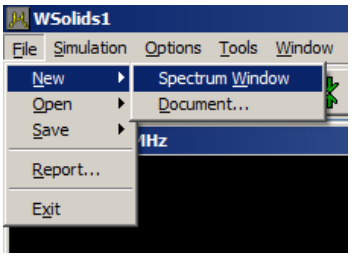
The menu system of WSolids1 consists of the following pop-up menus:



File (p. 17)	File and document management
Simulation (p. 28)	Simulation models and parameters management
Options (p. 39)	Change appearance, set title
Tools (p. 41)	Calculational and processing tools
Window (p. 46)	Multiple document management
Help (p. 47)	Help and program version information

2.1 File Menu

The File pop-up menu consists of the following items:



New Spectrum Window (p. 17)	Opens a new spectrum window
New Document... (p. 17)	Closes and removes existing spectrum windows or spin systems
Open (p. 18)	Opens a submenu to retrieve an experimental (p. 18) or calculated (p. 22) spectrum or a WSolids1 document (p. 22) or spin system (p. 22)
Save (p. 22)	Opens a submenu to save a spectrum (p. 22) or a WSolids1 document (p. 23) or spin system (p. 23)
Report (p. 24)	Opens to help file explaining how to generate reports
Exit (p. 27)	Exits WSolids1

2.1.1 New Document...

The **New document...** item of the File (p. 17) pop-up menu closes all spectrum windows and removes all spin systems in order to create a new starting point.

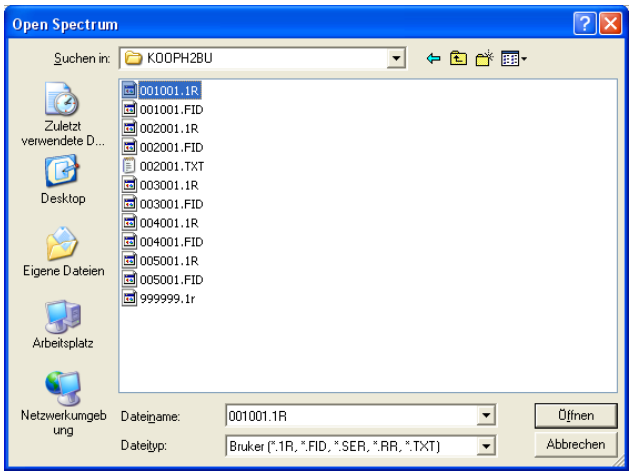
2.1.2 New Window

The **New window** item of the File (p. 17) pop-up menu creates a new spectrum window in the MDI client area of WSolids1.

A spectrum window is required to display experimental and calculated spectra. All actions are usually performed for the currently active spectrum window. For example, retrieving a spectrum file from hard disk automatically replaces the experimental spectrum of the currently active spectrum window.

Some actions automatically generate a new window, if they require a spectrum window in order to succeed and no active window exists. For example, retrieving a spectrum file will automatically load the spectrum into a new window, if no window has the input focus. However, if a spectrum window has the focus, WSolids1 will load and display the spectrum in this window.

2.1.3 Open Spectrum



The **Open Spectrum** item of the File (p. 17) pop-up menu retrieves an experimental spectrum into the Spectrum Window (p. 17) having the focus.

If the currently active spectrum window already contains an experimental spectrum, it is replaced by the new one. If no active spectrum window exists, a new spectrum window is created automatically.

Reading an experimental spectrum automatically changes the default parameters (p. 28) for the theoretical spectrum (of course, they can be modified afterwards).

Various formats of experimental spectra are recognized automatically by WSolids1. Please note that the file type option only determines which files are listed in the selection window and does not affect the way the selected file is treated. WSolids1 will always rely on its own strategy to determine the file type. Thus, in order to be recognized, the spectrum needs to follow a certain pattern, as detailed below for each file format.

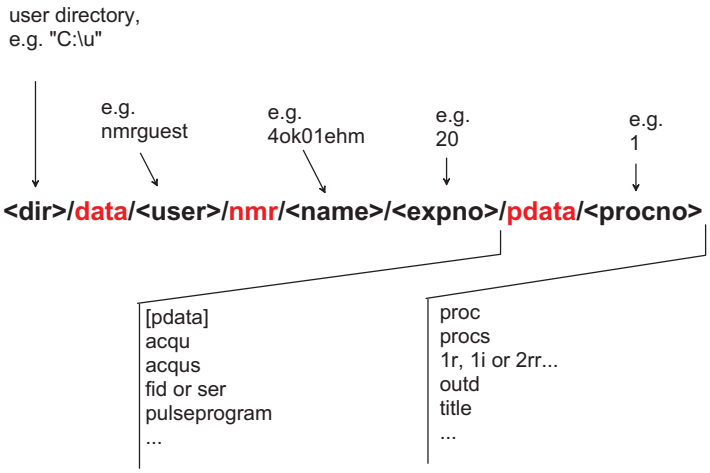
These are the file formats recognized by WSolids:

Spectrum format	Characteristics
TopSpin/XWinNMR (p. 19)	Requires an 1r file in floating point (or integer) format and the parameter files acqus and procs in JCAMP-DX format.
WINNMR generic (p. 19)	Requires an .1R or .FID file in floating point format and the parameter files .aqs and .fqs in binary format.
WINNMR UNIX (p. 20)	Requires an .1R or .FID file in floating point format and the parameter files .AQS and .FQS in ASCII format
WINNMR-ASCII (p. 20)	Reads a spectrum file in ASCII format generated by Bruker's WinNMR version 5.1 or later; it requires a single file, usually with the extension .TXT
Spinsight (p. 20)	Reads a Chemagnetics Spinsight file
SOLIDS (p. 21)	requires an ASCII file with header, followed by intensity data (preferred extension .dat)
JCAMP-DX (p. 21)	requires an ASCII file that follows the JCAMP-DX standard (preferred extension .dx)

Simpson (p. 22)	requires an ASCII file in Simpson format
Varian (p. 22)	some notes on how to deal with Varian datasets

Bruker TopSpin / XWinNMR

Spectra stored in Bruker's TopSpin or XWinNMR file format consist of a series of files stored in a convoluted directory structure, as indicated in this figure:



Those parts of the path name written in red letters are fixed names that are required by TopSpin/XWinNMR. A data set of name `<name>` consists of one or more spectra, each characterized by its experiment number `<expno>`, an integer. Each spectrum can have different processed data, stored in the `pdata` subdirectory under a specific processing number `<procno>`, an integer that is usually 1.

In order to be recognized by WSolids as TopSpin/XWinNMR file, the data files need to adhere to the following format:

- **1r** in binary floating point format needs to be present;
- **procs** needs to be present in the same directory, and **acqus** two levels higher; both are ASCII parameter files of variable record length and start with **##** (JCAMP-DX format), the **acqus** file contains the parameters **SFO1**, **SW_h**, **O1**, **AQ_mod**, **BYTORDA**, **TD**, **DECIM**, **DSPFVS**, **NC**, **NUCLEUS** and **procs** contains **OFFSET**, **SI**, **XDIM**, **BYTORDP**, **NC_proc**.

Bruker WINNMR Generic

This was the file format used by BRUKER's WIN-NMR version 4.0 (1D version), and is still produced by Bruker's GetFile utility if conversion of Aspect files is selected (basically, the parameter files are in binary format).

In order to be recognized by WSolids1 as a generic WINNMR file, the data files need to adhere to the following format, where *eee* stands for the three-digit **experiment number** and *ppp* for the three-digit **processing number**, each zero-padded if necessary. Thus, an experiment number of 2 and a processing number of 1 would result in the file name 002001. (WSolids1 itself doesn't care about the eeeppp format).

- *eeeppp*.**1R** or *eeeppp*.**FID** in binary floating point format need to be present (currently, WSolids1 does not read FID's)
- *eeeppp*.**AQS** and *eeeppp*.**FQS** need to be present in the same directory; these parameter files are in binary format of fixed record length and start with **A000**, the AQS file contains the parameters **SFO1**, **SW_h**, **O1** and FQS contains **SR**

Bruker WINNMR UNIX

This file format is similar to the generic WIN-NMR (p. 19) file format, however, the parameter files are of ASCII type and correspond to those generated by UXNMR and XWin-NMR. **WSolids1 uses this file format itself to store calculated spectra if the output format WIN-NMR is selected.**

In order to be recognized by WSolids as UNIX-type WINNMR file, the data files need to adhere to the following format:

- *eeeppp*.**1R** or *eeeppp*.**FID** in binary floating point format need to be present (Note that generic UXNMR files have these data stored as long integers; potentially, if coming from an SGI, the Endianness could also be different. If such a file is read, WSolids1 attempts to detect and convert them automatically; currently, WSolids1 does not read FID's)
- *eeeppp*.**AQS** and *eeeppp*.**FQS** need to be present in the same directory; they are ASCII parameter files of variable record length and start with **##** (JCAMP-DX format), the AQS file contains the parameters **SFO1**, **SW_h**, **O1**, and FQS contains **OFFSET**

Bruker WINNMR ASCII

WinNMR is able to export spectra in ASCII format; depending on the version of WinNMR, slight differences arise. The file starts with some parameters, one on each line, and is then followed by pure intensity data, each point on its own line. Here is the beginning of such a file:

```
Data file: D:\NMR\ASP3000\KOPOPH3\101001.TXT
Starting Point: 0
Ending Point: 4095
Point Count: 4096
Real Data
SFO1: 81.018000 MHz
SF: 81.023633 MHz
Offset: 444.735199 ppm
Decim: 0
Dspfvs: 0
FW: 100000.000000 Hz
Sweep Width: 83333.333332 Hz
Hz/Pt: 20.345052
First Point: 36034.061368 Hz
Last Point: -47299.271964 Hz
First Point: 444.735199 PPM
Last Point: -583.771308 PPM
AQmod: 2
-5759
-1961
...
```

Chemagnetics SpinSight

The Spinsight data format consists of several component files all contained within one directory.

In order to be recognized by WSolids as SpinSight file, the data files need to adhere to the following format:

- **data**: this is a binary file which contains the actual NMR data. The storage order is: all real values followed by all imaginary values, i.e., the data are unshuffled. No formating, end of row or end of file characters are present in this file.
- **acq**: this is a text file describing the acquisition parameters used in acquiring the data file. These parameters can also be used for a prescription on how to acquire NMR data. The meaning of the acquisition parameters depends on the definitions used in the associated pulse program. WSolids1 is mainly interested in **SF** and **SW**.

- **proc**: this is a text file containing parameters which describe the current state of the data file and the previous operations that have been performed on the data since it was acquired. WSolids1 is mainly interested in **datatype**, **domain1**, **current_size1**, **rmp1**, **rmv1**, **rmvunits1**.

SOLIDS

This type of file format is produced by Solids, the FORTRAN predecessor of WSolids1, and was created to allow a slightly more general interface in terms of file formats. ASCII files created by WIN-NMR require only minor editing of the file header in order to conform to this format (the text and some lines need to be deleted).

In order to be recognized by WSolids1 as SOLIDS file, the **ASCII** data file need to adhere to the following format, where each parameter is on a separate row:

- number of points (SI)
- spectrometer frequency in MHz (SF)
- digital resolution in Hz per point ((F1 - F2) / SI)
- highest frequency, i.e. frequency of first point in Hz (F1)
- lowest frequency, i.e. frequency of last point in Hz (F2)
- intensity data as integers or floating point numbers, each in a separate row

JCAMP-DX

The JCAMP-DX (Joint Committee on Atomic and Molecular Physical Data Exchange) format has been initiated by IUPAC to achive better long-term archival and exchange of spectroscopic data. The main features [1] are:

- first non-binary approach ever
- vendor independent, JCAMP is not owned by anybody
- printable characters only (important for e-mail etc.)
- reasonable compression rates (long before LHARC etc. did show up)
- extendable and open definitions to allow further improvements

In my opinion, this was a good idea, in principle. However, in practice, the standard is too unclear in several aspects, thus writing an import filter for such data is a royal pain. The advantage, however, is that WSolids1 using the JCAMP-DX route, can use any file format that Kirk Marat's `SpinWorks` (`ftp://davinci.chem.umanitoba.ca/pub/marat/SpinWorks/`) can process!

WSolids1 checks for the following parameters: **TITLE**, **JCAMP-DX** (with values of 4.24, 5.00, or 5.01), **DATA TYPE**, **NPOINTS**, **.OBSERVE FREQUENCY**, **FIRSTX**, **LASTX**, **XFACTOR**, **DATA CLASS**. Currently, only XY-DATA are supported.

References:

(1) posting by Dr. Michael Grzonka in the newsgroup bionet.structural-nmr, Subject: The JCAMP standard of spectroscopic data transfer - a summary, on 29 January 1996.

(2) McDonald, Wilks, *Appl. Spectrosc.* **1988**, *42*, 151

(3) Davies, Lampen, *Appl. Spectrosc.* **1993**, *47*, 1093

(4) Lampen, Lambert, Lancashire, McDonald, McIntyre, Rutledge, Fröhlich, Davies, *Pure Appl. Chem.* **1999**, *71*, 1549, DOI: 10.1351/pac199971081549.

Simpson

"SIMPSON: A General Simulation Program for Solid-State NMR Spectroscopy" was the title of the paper that introduced SIMPSON. Its output is an ASCII text file, usually with extension .SPE. WSolids1 requires the parameters **SIMP**, **NP**, **SW** and, in newer versions, **REF**.

The Simpson spectrum file format does not contain sufficient information for proper referencing, in older versions not even the measurement frequency, therefore WSolids1 asks you for SF; newer versions of Simpson produce an output file that contains the REF parameter. Anyway, this information is not sufficient. I will think about a solution to this problem, but, honestly, it is a problem caused by Simpson.

Also, the spectrum produced by Simpson is reversed unless you use the statement "conjugate_fid false" in the par section of your Simpson input file. To flip your spectrum around, you can use WSolids1 Tools—reverse spectrum.

Currently, I would suggest the following procedure:

1. read the Simpson spectrum into WSolids1, specify **sfo1** of your experimental spectrum
2. reverse the spectrum
3. save in TopSpin format
4. use TopSpin to change the referencing.

Reference:

- M. Bak, J. T. Rasmussen, N. C. Nielsen, *J. Magn. Reson.* **2000**, *147*, 296, DOI: 10.1006/jmre.2000.2179.

Varian

Reading of Varian files has been planned but discarded after reading the Varian documentation. The reason is that Varian actually does not save the processed spectrum, only the processing instructions to get there. Therefore, the reading of Varian files would involve the implementation of all the necessary processing steps. Because there is already nice processing software available freely, namely Kirk Marat's SpinWorks (see information on JCAMP-DX (p. 21)), my efforts will be reduced to ensuring that users of SpinWorks will be able to read the JCAMP-DX files exported in SpinWorks into WSolids1.

2.1.4 Open as Calculated Spectrum

Besides reading an experimental spectrum, this feature allows to read a second spectrum into the memory reserved for the calculated spectrum for the purpose of dual display. Carrying out a calculation will replace this spectrum by the calculated spectrum (in memory, not on disk).

2.1.5 Open WSolids Document

The WSolids document is a self-contained document providing experimental and calculated spectra as well as spin systems with their required parameters.

2.1.6 Open WSolids Spin System

This menu action retrieves only the spin system part from a WSolids1 XML document. You have the choice of discarding all already existing spin systems or of adding to them.

2.1.7 Save Spectrum

The **Save Spectrum** item of the File (p. 17) pop-up menu saves a spectrum from the active Spectrum Window (p. 17). If the spectrum window contains only an experimental spectrum, the experimental spectrum is saved. If there is a calculated spectrum available, the calculated spectrum is always saved.

There are several output formats available:

1. a WinNMR (p. 20) file with UNIX-type ASCII parameter files;
2. in TopSpin/XWinNMR (p. 19) format;
3. in Solids (p. 21) format;
4. in ASCII format as rows of frequency, intensity data;
5. in JCAMP-DX (p. 21) format (only as uncompressed XYDATA in X++(Y..Y) format).

When writing WinNMR files, the file name should adhere to the eeeppp.* (p. 19) convention.

When writing Topspin files, please consider that the dialog was written initially for WinNMR. Therefore, if you want to create the file `d:\u\data\nmrguest\nmr\simulation\11\pdata\20\1r`, you should point the path to the `...\simulation` subdirectory and enter the file name `011020` (file type Topspin). WSolids1 extracts from this file name the corresponding experiment and processing numbers.

Also, because Topspin data are stored as integers you should scale up (p. 44) the calculated spectrum before saving.

> **Note:** When displaying experimental spectra and spectra calculated by WSolids1 in WinNMR and the calculated spectrum has not been scaled (p. 44) to match the amplitude of the experimental spectrum, use the "relative intensities" scaling mode of the dual/multiple display window.

2.1.8 Save WSolids Document

The WSolids document is a self-contained document providing experimental and calculated spectra as well as spin systems with their required parameters.

2.1.9 Save WSolids Spin System

Saves the spin system only as a WSolids XML document file.

2.1.10 Report

Quick guide to generate a report:

- copy or write your WSolids1 XML document into the directory containing the style sheets
- open this copy of your XML file in your web browser

WSolids1 does not have a feature to create fancy resports. Instead, this menu option opens the help file at the current section. Here, I am explaining the steps required to generate a report from your WSolids1 XML document. On first sight, it may seem complicated, but once everything is in place it is not too hard. Depending on the version of WSolids1 that you are using, it may have shipped with all the necessary style files, otherwise you can download the required files from the WSolids1 home page (http://anorganik.uni-tuebingen.de/klaus/soft).

The WSolids1 XML Document

Extensible **M**arkup **L**anguage, XML (http://www.w3.org/TR/2006/REC-xml11-20060816), is a text file format that can be used to represent data in a structured way. It is human readable (in contrast to binary files), and in many cases human understandable. However, although the file itself is readable it doesn't make for good reading! But there are tools available that help to present the data in a more convenient way. For example, your favorite web browser should be able to deal with a XML file. The following steps explain the procedure.

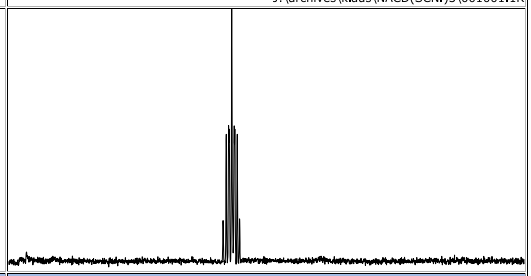
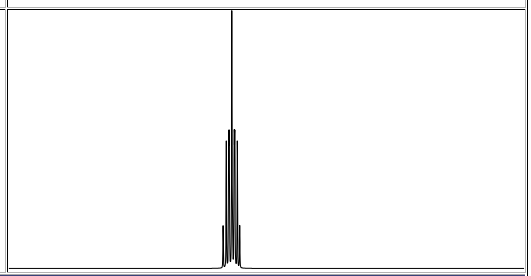
The excerpt from a WSolids1 XML document shown below illustrates the concept of human readability, but you may also notice that the content is not always understandable. If your web browser does not know how to deal with the XML file, this will actually be the way it will display the WSolids1 document to you:

```
<?xml version="1.0" encoding="ISO-8859-1"?>
<?xml-stylesheet type="text/xsl" href="wsolids.xsl" ?>
<wsolids>
 <creator>Wsolids1</creator>
 <creatorversion>1.20.12</creatorversion>
 <display>
  <count>1</count>
 <window>
  <id>1</id>
  <type>dual</type>
  <spectrum>
   ...
```

The XSLT Transformation

What is required is a way to tell the browser how to deal with the document, i.e., how to translate the data. This objective is achieved by using so called **E**xtensible **S**tylesheet **L**anguage **t**ransformation, XSLT. Versions of WSolids1 of 1.20.15 and above write a reference to the necessary XSL file as second line of the XML file. If this line is not present, you need to add it manually (use a text editor such as the Windows Editor, Notepad or similar, and not a word processing software such as office or other desktop publishing software, and you can copy and paste the line displayed in red in the figure above).

The XSL file will help the browser to turn the XML entries into something that it is used to present, i.e., HTML data. In principle, this is sufficient, but to make the result more fancy we can use a style sheet to tell the browser how to format things. This information is contained in the file with the extension .css (= **c**ascading **s**tyle **s**heets), and the result should look like this:

Wsolids1 (1.20.12) Document	
spectrum 1 of 1	
type:	**expe**
si:	4096
td:	4096
sf:	44.391041
f1:	17362.884766
f2:	-494.257813
file:	J:\archives\klaus\NACD(SCN.)3\001001.1R
plot	
type:	**calc**
si:	4096
td:	4096
sf:	44.391041
f1:	17362.884766
f2:	-494.257813
file:	
plot	
spin system 1 of 1	
relative intensity:	100.000000%
tied to previous site:	no
model:	Multi Spin
WSolids1 model:	MAS: Spin-1/2 -- Spin-S (Stick)

Scalable Vector Graphics

This report demonstrates that XSL is also able to generate graphics from XML data. Here, I am using XSL to turn the data into **S**calable **V**ector **G**raphics, SVG. The SVG format is supported natively by the Mozilla family of browsers, **FireFox** and **SeaMonkey**. SeaMonkey is my favorite web browser because I have been using Netscape Communicator for ages and SeaMonkey follows the Communicators' philosophy of integrating browser, email, newsreader, and HTML editor. Other web browsers, such as Microsoft **Internet Explorer** before version 9, may require a plugin to be able to display SVG graphics, e.g., the Adobe SVG viewer plugin. **Internet Explorer 9** also supports SVG, but of course in a way different from other browsers :-(Therefore I am providing two flavours of those XSL files that generate the SVG output, one version for IE 9 (`wsolids_display_ie9.xsl`) and another version for all other browsers (`wsolids_display_moz.xsl`). Depending on the browser that you want to use, copy either `wsolids_display_ie9.xsl` or `wsolids_display_moz.xsl` to `wsolids_display.xsl`. The default installation will be for non-IE9 users!

The advantage of SVG is that it prints rather well, compared to bitmapped pictures (e.g., JPEG, GIF, or PNG). You can verify this if you zoom in on the graphics shown in the report above (many spectra shown in publications will look worse)! In case you don't want the SVG graphics to be included in the report, either because your browser does not support this or you don't want to wait the time required by the browser to process the graphics, you can disable them. Open the file `wsolids_display.xsl` in your text editor of choice:

```
<?xml version="1.0" encoding="iso-8859-1"?>
<xsl:stylesheet version="1.0" xmlns:xsl="http://www.w3.org/1999/XSL/Transform"
                              xmlns:svg="http://www.w3.org/2000/svg">

<xsl:param name="UseSVG" select="1"/>

<xsl:template match="display">
   <xsl:apply-templates />
</xsl:template>
```

and change in the line printed in red the 1 to a 0: <xsl:param name="UseSVG" select="0"/>.

Links to the software mentioned:

- FireFox: http://www.mozilla.org/en-US/
- SeaMonkey: http://www.seamonkey-project.org/
- Adobe SVG viewer plugin: http://www.adobe.com/devnet/svg/adobe-svg-viewer-download-area.html

Location of Required Files

For security reasons, the XML file and the required XSL and CSS helper files need to reside in the same directory. New distributions of WSolids1 will bundle these helper files in a subdirectory report of the WSolids1 program directory. If you cannot write to this subdirectory because of limited access rights, maybe you can copy them to a location where you have write access, or you can download the helper files from the WSolids1 home page and install them there. My recommendation is to create a WSolids subdirectory in your Own documents place and store all data there.

With all the files at the same place, simply drag the XML file into your browser or open it from the browser's file menu.

Creating HTML Files Permanently

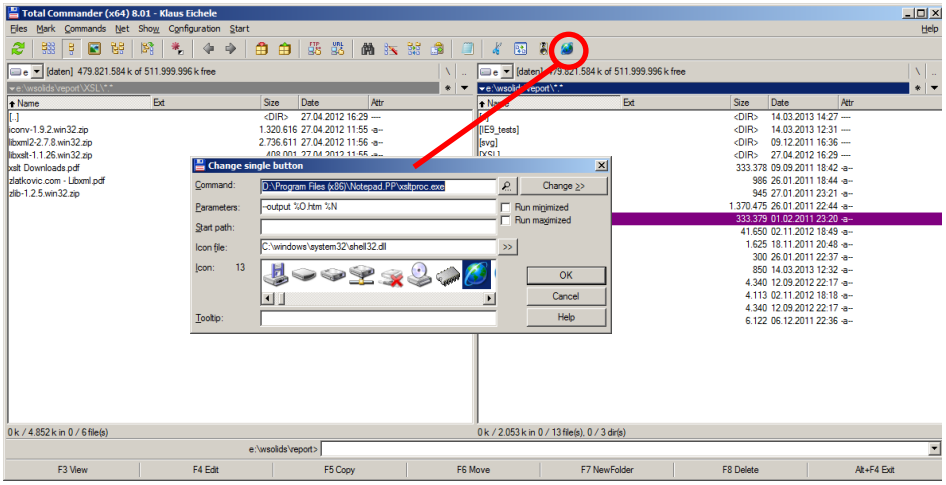
Note: There is no point in saving the displayed report from your browser, because this will save the original XML file rather than the generated HTML version. To permanently generate an HTML version, you need an XSL processor, e.g. xsltproc Alternatively, SeaMonkey will give you the HTML version if you select File|Edit Page!

There could be reasons for wanting a permanent HTML version of the report (e.g. to import and modify it with word processing software; unfortunately, they will not display the graphics). Unless you are using SeaMonkey as browser anyway, you will need additional software such as an XSL processor to achieve this. In combination with such an excellent file manager as TotalCommander (shareware, well worth the money!), the conversion is as easy as hitting a custom button on a toolbar. This section will describe one way to achieve this.

First, download a Windows version of the libxml package (xsltproc mentioned above is part of this download). In particular, you will need the following libraries: libxml2, libxslt, iconv, zlib. In principle, you can unpack the files in any location, you need the files in the bin folders of the zip archives. If you have administrator rights, program files\libxml could be a good place for these files, otherwise own documents\libxml. For some reason, xsltproc gobbles up the HTML output if the Mozilla version of the XSL file is used; with the IE9 version, the resulting HTML works with the Mozilla browsers and IE9. Using the command line, you could perform conversions like this:

```
"c:\Program Files (x86)\libxml\xsltproc.exe" --output mydocument.htm mydocument.xml
```

Secondly, if you want to use Totalcommander, you can add a custom button to the toolbar. Place the mouse pointer on the toolbar, hit the right mouse button and select “change”. Enter the information as shown below, adjusting the path to `xsltproc.exe` to your installation:



Now you can select the XML file you want to convert and hit your custom button!

Links to the software mentioned:

- xsltproc: `http://xmlsoft.org/XSLT/`
- libxml: `http://www.zlatkovic.com/libxml.en.html`
- SeaMonkey: `http://www.seamonkey-project.org/`
- TotalCommander: `http://www.ghisler.com/`

2.1.11 Exit

The **Exit** item of the File (p. 17) pop-up menu quits WSolids1. All existing data will be lost, if not saved prior to selecting Exit.

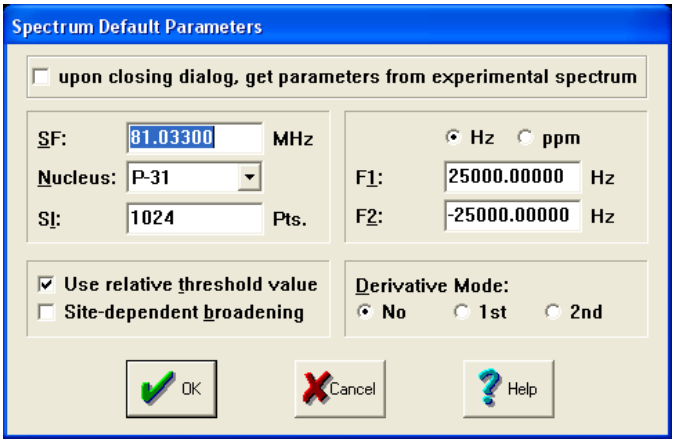
2.2 Simulation Menu

The Simulation pop-up menu consists of the following items:

Item	Purpose
Default parameters (p. 28)	Invokes a dialog box to retrieve parameters for the calculated spectrum
New site (p. 35)	Allocates and adds a new site to the calculational model
Edit sites (p. 37)	Manage sites, modify parameters etc.
Calculate (p. 38)	Performs a calculation using the currently selected simulation models and parameters
Active window only (p. 38)	Perform calculation for currently active spectrum window only or for all spectrum windows
Cycle through (p. 38)	Calls the next step in the Input-Calculate-Display cycle
Cycle options (p. 38)	Customize the cycle steps

2.2.1 Spectrum Default Parameters

The **Default parameters** item of the Simulation (p. 28) popup menu invokes the Spectrum Default Parameters dialog box. The default parameters characterize the appearance of the calculated spectrum; they apply to all sites.



The default parameters define:

Parameter	Purpose
Nucleus (p. 29)	Observed nucleus
SF (p. 29)	Spectrometer frequency (Larmor frequency) in MHz
SI (p. 30)	Size of calculated spectrum in points
ppm/Hz (p. 30)	Toggles input for F1/F2 between Hz or ppm
F1 (p. 30)	High-frequency limit of calculated spectrum
F2 (p. 30)	Low-frequency limit of calculated spectrum
Use relative threshold value (p. 31)	Toggle between use of a threshold value in the convolution or doing the full convolution
Site-dependent broadening (p. 31)	Individual or global line broadening
Derivative Mode (p. 34)	Absorption or derivative display
Get Experimental Parameters (p. 29)	Upon Closing, Get Parameters From Experimental Spectrum

Upon Closing, Get Parameters From Experimental Spectrum

If this checkbox is activated, WSolids1 will retrieve SF, F1, F2 and SI from the experimental spectrum and update the parameters of the calculated spectrum accordingly. This will invalidate the content of the calculated spectrum and require a new calculation.

When reading an experimental spectrum its parameters will be used to initialize the calculated spectrum. However, you are free to modify those of the calculated spectrum any time. In fact, for some calculation models it is advisable to narrow down the limits of the calculated spectrum to the region of interest. If, however, for some reason experimental and calculated spectrum should have the same size and limits, this option will be useful. Also, changing the referencing (p. 45) of the experimental spectrum could also necessitate this reinitialization.

Observed Nucleus

The kind of observed nucleus is selected in the Spectrum Default Parameter (p. 28) box.

In many cases, the actual selection here is not important. Exceptions are, for example:

- Observation of a quadrupolar nucleus (here, the nuclear spin quantum number is important)
- If a quadrupolar nucleus is coupled to the observed nucleus, the ratio of magnetogyric ratios of both nuclei is used to calculate the Larmor frequency of the quadrupolar nucleus

Spectrometer Frequency

The parameter SF defines the spectrometer or Larmor frequency in MHz and is set in the Spectrum Default Parameter (p. 28) box.

Actually, this value corresponds to the **frequency of the chemical shift reference compound**, and thus not to SFO1 as used in Bruker parameter files. On newer versions of TopSpin, BFO1 should correspond to this value if the IUPAC 2001 recommendations of relative frequencies have been imple-

mented. If your experimental spectrum has been re-referenced, use SF of the processing parameters (note that the DisMSL/DISNMR acquisition parameter SF has a different meaning).

If an experimental spectrum is available, this parameter is set by default and should not be changed. This value is used in the conversion of ppm into Hz and vice versa. For the direct observation of quadrupolar nuclei, its magnitude relative to the quadrupolar coupling constant is important for the observed line shape.

Valid values for the "spectrometer frequency" are any positive, non-zero floating point numbers.

> **Note:** All calculations assume that the Zeeman interaction is the dominant interaction (high-field approximaton). For example, calculation of a Pake doublet with a dipolar coupling constant of 1 kHz and a spectrometer frequency of 100 Hz will not give the proper result! The high-field approximation is slightly relaxed in cases involving quadrupolar nuclei, but one should always be aware of the approximations behind any type of calculation!

Spectrum Size

The spectrum size **SI** defines the size of the calculated spectrum in points and is set in the Spectrum Default Parameter (p. 28) box. Traditionally, its values are multiples of two, but it is not limited to these numbers. If an experimental spectrum is available, this parameter is set by default.

Together with the high- and low-frequency limits, F1 (p. 30) and F2 (p. 30), the spectrum size determines the spectral resolution. Often, it is sufficient to use the same spectral resolution as the experimental spectrum. However, in cases involving "stick" approaches, a higher digital resolution for the calulated spectrum is advisable.

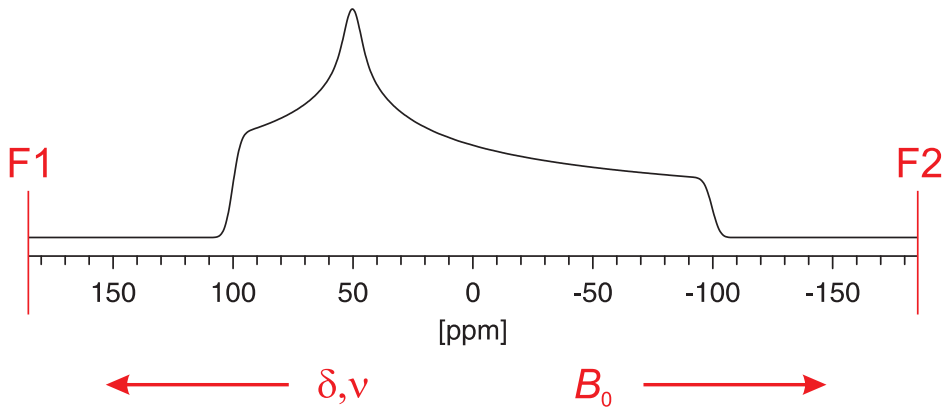
The spectrum size affects the time required for calculating a spectrum, i.e., the performance of the interpolation routine for the powder averaging or the convolution routine depends on the digital resolution.

Valid values for the spectrum size are positive integers greater than or equal to 16. Additionally, the letter **K** can be used to indicate Kilo-points, 1K = 1024 points.

ppm / Hz

The two mutually exclusive radio buttons **ppm** and **Hz** in the Spectrum Default Parameter (p. 28) box allow to toggle the input between frequency (Hz) or chemical shift (ppm) units. In order to perform the conversion, the value presently selected for the spectrometer frequency (p. 29) is used.

Spectrum Limits



The spectrum limits are specified by the high-frequency limit (in conventional NMR, the "left" limit), **F1**, and the low-frequency limit, **F2**, in the Spectrum Default Parameter (p. 28) box. Dependent on

the state of the radio buttons ppm/Hz (p. 30), the input is taken in units of ppm or Hz. To perform the conversion between ppm and Hz, the current value of SF (p. 29) is taken. In combination with SI (p. 30), these parameters determine the digital resolution.

Use Relative Threshold Value

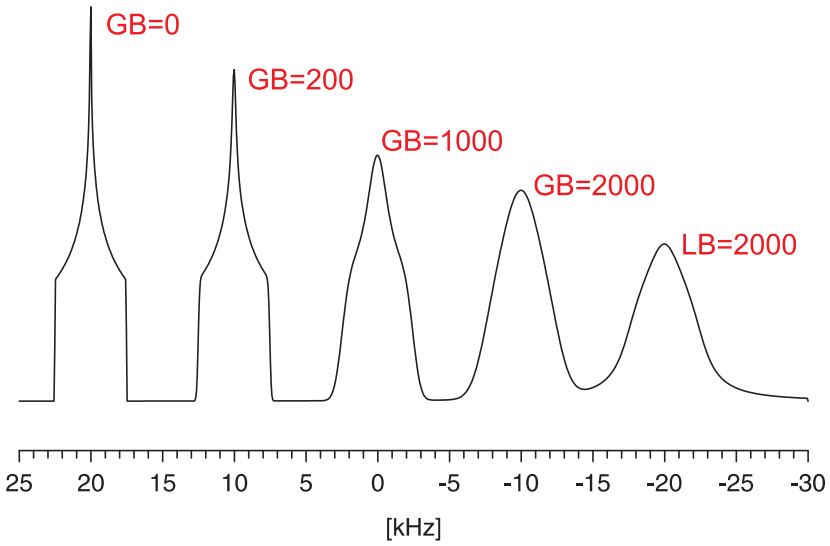
In the Spectrum Default Parameter (p. 28) box, the status of the checkbox for using relative threshold values determines the time required to do a convolution.

Checkbox status	Meaning
☐	The mixed Gaussian-Lorentzian line shape used in the convolution process is used until the intensity of the wings reaches zero. This is the more lengthy process but may be required if weak peaks are to be displayed in the presence of very strong peaks.
☑	The mixed Gaussian-Lorentzian line shape used in the convolution process is used until the intensity of the wings reaches 1/10000 of the greatest spectral intensity. This reduces calculation time but may produce funny looking line shapes for weak peaks.

Site-Dependent Broadening

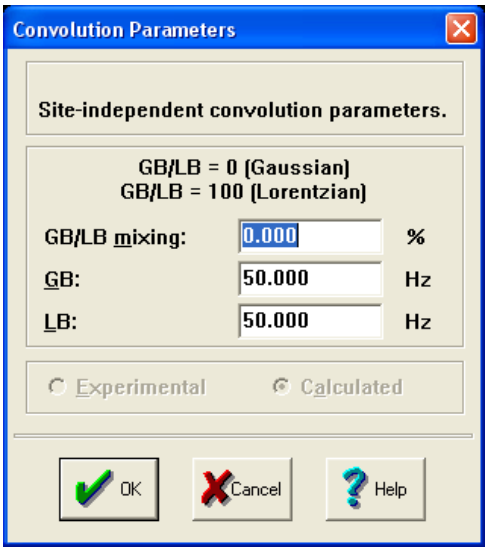
In the Spectrum Default Parameter (p. 28) box, the status of the checkbox for **site-dependent broadening** determines whether each site requires its own set of convolution parameters (p. 32). Because the Gaussian / Lorentzian peaks used for convolution are normalized, the relative areas of each site are approximately preserved.

Checkbox status	Meaning
☐	Usually, the selection of no site-dependent broadening will do. In this case, only one set of convolution parameters will be necessary. The convolution routine is activated only once, after all site specific spectra have been calculated.
☑	In this case, each site requires its own set of line broadening parameters. Also, the convolution routine is invoked each time after a site specific spectrum has been generated.



Note: Although the convolution parameters belong to the spectrum window (spectra at different spectrometer frequencies will require different broadening), the actual parameters are accessible via the spin system.

2.2.2 Convolution Parameters



The convolution parameters determine the amount of "line broadening" added to the calculated spectrum.

The convolution parameters should not be mixed up with the LB/GB parameters used in apodization functions applied to experimental spectra. Here, they take into account the sum of all line broadening effects intrinsic to the sample and the spectrometer (and processing). Such effects can be inhomogeneity of the external magnetic field, homonuclear dipolar couplings, unresolved indirect couplings, interactions with quadrupolar nuclei, degree of crystallinity (chemical shift dispersion), insufficient decoupling power, temperature gradients, etc. etc., and finally the actual window function applied to the experimental data. In short, the convolution parameters represent all these effects in a phenomenological manner.

Convolution is done in the frequency domain, rather than in the time domain. Exponential multiplication in time domain requires for N points N multiplications; in contrast, the equivalent in the

frequency domain — convolution with a Lorentzian peak — requires $N \times (N-1)$ multiplications, unless a threshold (p. 31) value is specified!

Although considered part of the spectrum parameters rather than of the spin system, access to convolution parameters is gained by editing the spin system. Convolution also depends on the setting of the site-dependent convolution (p. 31) check box in the Spectrum Default Parameter (p. 28) box.

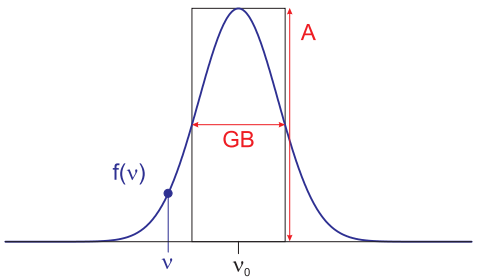
Parameter	Purpose
GB/LB mixing (p. 33)	The GB/LB mixing in percent determines the amount of Gaussian- Lorentzian character of the convolution function: 0: pure Gaussian 100: pure Lorentzian
GB (p. 33)	Gaussian broadening in Hz
LB (p. 34)	Lorentzian broadening in Hz

Gaussian/Lorentzian Mixing

In the Convolution Parameters (p. 32) dialog box, the Gaussian/Lorentzian mixing determines the weighting of Gaussian and Lorentzian line shapes in the convolution subroutine. A value of 0 % corresponds to a pure Gaussian line shape, a value of 100 % yields a pure Lorentzian line shape. In the case of mixed line shapes, both Gaussian broadening, GB (p. 33), and Lorentzian broadening, LB (p. 34), must be specified, but can be different.

> **Note:** If calculations are performed in the frequency domain, Lorentzian line shapes require considerably longer computation times because their wings extend much farther than those of Gaussian peaks. For time domain convolution, both line shapes require the same time. In the case of frequency domain convolution, the subroutine uses a threshold (p. 31) value, 0.00001 of the maximum intensity, to reduce computation times. This, however, can create funny artefacts, therefore you can disable this threshold value.

Gaussian Convolution



In the Convolution Parameters (p. 32) dialog box, the value of **GB**, in Hz, specifies the full width at half maximum-height of a Gaussian peak. This line shape will be employed in the convolution of spectra.

The intensity at a given frequency is given by the following expression for an absorption-mode Gaussian:

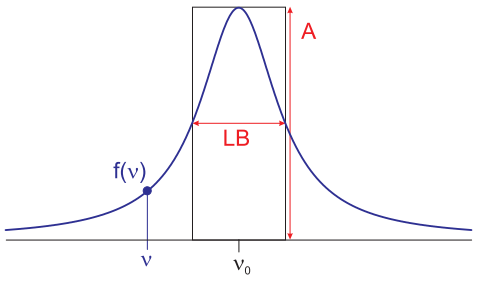
$$f(\nu) = A \exp\left[\frac{-4\ln(2)(\nu-\nu_0)^2}{GB^2}\right]$$

where:

A : peak maximum amplitude
ν_0 : peak centre frequency
GB : full width at half maximum-height

In order to preserve the relative areas of sites with different line broadening parameters, the convolution procedure takes into account that the area of a Gaussian peak can be approximated by $\sqrt{\pi/4\ln 2} \times A \times GB = (1.064467 \times A \times GB)$.

Lorentzian Convolution



In the Convolution Parameters (p. 32) dialog box, the value of **LB**, in Hz, specifies the full width at half maximum-height of a Lorentzian peak. This line shape will be employed in the convolution of spectra.

The intensity at a given frequency is given by the following expression for an absorption-mode Lorentzian:

$$f(\nu) = \frac{A}{\left[1+\frac{4(\nu-\nu_0)^2}{LB^2}\right]}$$

where:

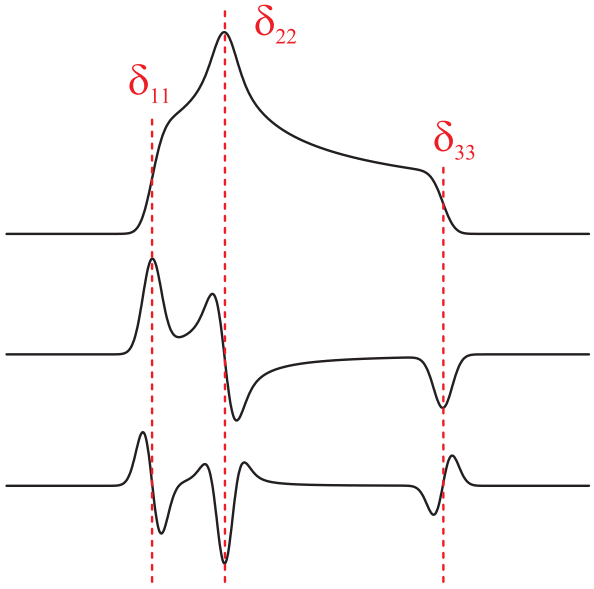
A : peak maximum amplitude
ν_0 : peak centre frequency
LB : full width at half maximum-height

In order to preserve the relative areas of sites with different line broadening parameters, the convolution procedure takes into account that the area of a Lorentzian peak can be approximated by $[(\pi/2) \times A \times LB] = 1.570796 \times A \times LB$.

2.2.3 Derivative Mode

In the Spectrum Default Parameter (p. 28) box, the status of the mutually exclusive radio buttons **Derivative: No/1st/2nd** determine whether the calculated spectrum will be displayed in normal (absorption) mode or as the first or second derivative.

Note: The experimental spectrum remains unaffected by this setting. Use your favourite NMR processing program to manipulate the experimental spectrum. (Taking the derivative of a spectrum dramatically decreases the signal-to-noise ratio. Modern processing software has usually some sort of digital filtering, e.g. Savitzky-Golay, implemented for generating derivatives of spectra. For calculated spectra, one can get away with a much simpler procedure.)



There are certain advantages in fitting the line shape in one of the derivative modes. In this mode, the frequencies of the singularities can be determined more accurately. As indicated in the picture, the points of inflection (e.g. δ_{11} and δ_{33}) correspond to peaks in the first derivative, while the discontinuities (e.g. δ_{22}) reveal themselves as peaks in the second derivative. The width of the peaks in the first derivative line shape indicates the natural line width, a parameter which can be employed in the convolution of the calculated spectrum.

References

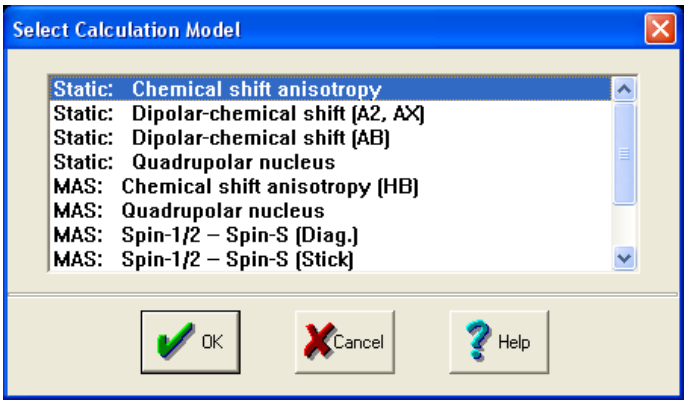
- T. G. Oas, C. J. Hartzell, T. J. McMahon, G. P. Drobny, F. W. Dahlquist, *J. Am. Chem. Soc.* **1987**, *109*, 5956, DOI: 10.1021/ja00254a010.
- T. G. Oas, C. J. Hartzell, F. W. Dahlquist, G. P. Drobny, *J. Am. Chem. Soc.* **1987**, *109*, 5962, DOI: 10.1021/ja00254a011.
- C. J. Hartzell, M. Whitfield, T. G. Oas, G. P. Drobny, *J. Am. Chem. Soc.* **1987**, *109*, 5966, DOI: 10.1021/ja00254a012.

2.2.4 New Site

A site is an independent part of a spectrum with a line shape uniquely defined by parameters (e.g. chemical shifts, couplings etc.) specific to the calculational model selected for this site.

The feature **New Site** of the Simulation (p. 28) popup menu adds a new site to the calculation model. It calls the Select Calculation Model (p. 36) dialog box and requests the user to select a model. Afterwards, it initiates the input of the appropriate site specific parameters.

2.2.5 Select Calculation Model

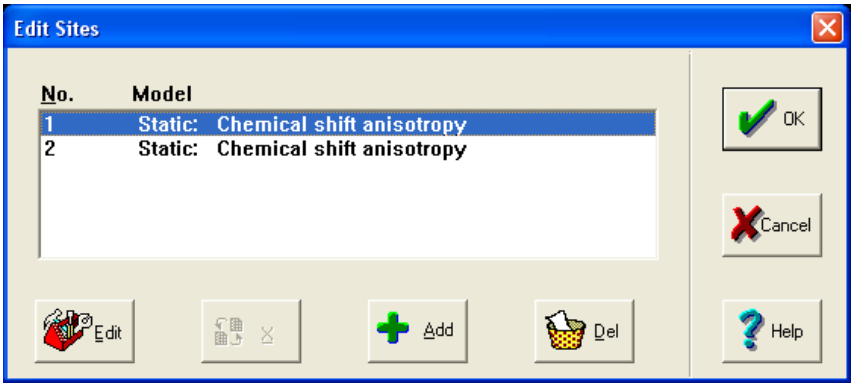


The **Select Calculation Model** dialog box, available from the New Site (p. 35) item of the Simulation (p. 28) popup menu, allows the user to select a calculational model from a list of available models. Each model is, in its performance, tailored to a specific situation. Currently, the following models are supported:

Model	Characteristics
Static: Chemical shift anisotropy (p. 50)	Spectrum of a static powder sample showing chemical shift anisotropy ("powder pattern")
Static: Dipolar−chemical shift (A2, AX) (p. 52)	Chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling for a homonuclear pair of equivalent spin-1/2 nuclei or a heteronuclear spin pair in a static powder sample (A2 or AX approximation)
Static: Dipolar-Chemical Shift (AB) (p. 55)	Chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling for a homonuclear pair of spin-1/2 nuclei, including "second-order" effects, in a static powder sample (AB)
Static: Quadrupolar Nucleus (p. 58)	Quadrupolar interaction up to second order for the observed nucleus, including chemical shift anisotropy, for a static powder sample. Optionally, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus)
Static: Three-Spin System (AMX) (p. 61)	not tested yet
MAS: Chemical shift anisotropy (HB) (p. 62)	Spectrum of a powder sample spinning at the magic angle, showing chemical shift anisotropy
MAS: Dipolar-Chemical Shift (A2, AX) (p. 64)	Chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling for a homonuclear pair of equivalent spin-1/2 nuclei or a heteronuclear spin pair in a static powder sample (A2 or AX approximation)

MAS: Quadrupolar nucleus (p. 65)	Spectrum of central transition of a quadrupolar nucleus in a powder sample spinning fast at the magic angle
MAS: Spin-1/2 – Spin-S (Diag.) (p. 67)	Considers spin-spin interactions with a quadrupolar nucleus under magic-angle spinning, using full matrix diagonalization
MAS: Spin-1/2 – Spin-S (Stick) (p. 70)	Considers spin-spin interactions with quadrupolar nuclei under magic-angle spinning, using first-order perturbation theory and "stick" approach
MAS: Spin-1/2 – Spin-S (Shape) (p. 74)	Considers spin-spin interactions with a quadrupolar nucleus under magic-angle spinning, using first-order perturbation theory to calculate line shape
VAS: Dipolar-chemical shift (A2, AX) (p. 76)	Considers chemical shift and spin-spin interactions for a homo- or heteronuclear pair of nuclei, i.e., A_2 or AX approximation, under variable-angle spinning
VAS: Dipolar-chemical shift (AB) (p. 78)	Considers chemical shift and spin-spin interactions for a homonuclear pair of nuclei, i.e., AB approximation, under variable-angle spinning
HR: Spin-1/2 Coupled to Quadrupolar Nucleus (Relaxation) (p. 80)	Considers a spectrum in solution (HR= high-resolution) of a spin-1/2 coupled to a quadrupolar nucleus showing the effect of relaxation

2.2.6 Edit Sites



The item **Edit Sites** of the Simulation (p. 28) popup menu allows to manage the sites constituting the calculational model. A dialog box provides a list of currently available sites.

Selection	Action
Edit	Highlight the desired site in the list box using mouse or keyboard and select the **Edit** button to obtain access to the parameters for this site. You can also **double-click** on the desired site to trigger this action.
Add	Select the **Add** button to add a new site to the calculational model.

Delete	Select the **Delete** button to delete the site highlighted in the list box. A dialog box requesting confirmation pops up before the site gets actually deleted. **There is no Undo function!**

Note: Access to editing the parameters of a spin system might be easier by using the cycle (p. 38) feature, i.e., hitting the Enter key the appropriate number of times.

2.2.7 Calculate

The item **Calculate** of the Simulation (p. 28) popup menu starts calculation of a theoretical spectrum, using the selected calculation models and site-specific parameters. If not all parameters were initialized, it calls the appropriate parameter dialog boxes. After a successful calculation, the calculated spectrum will be displayed. If there is no spectrum window currently active, this procedure also opens a spectrum window and asks for default spectrum parameters. The detailed calculation mode depends on the state of the Active only (p. 38) menu item.

2.2.8 Active Only

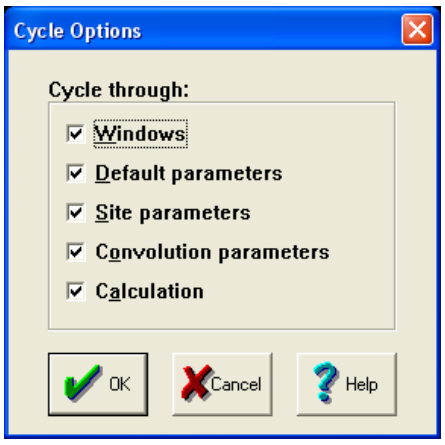
The item **Active only** of the Simulation (p. 28) popup menu determines if a calculation is performed for the currently active window only or for all available spectrum windows.

2.2.9 Cycle

The item **Cycle** of the Simulation (p. 28) popup menu automatically initiates the next step in the generation of a calculated spectrum to refine the agreement between experimental and theoretical spectra. The detailed course of the cycle feature depends on the selections made under Cycle options (p. 38).

Note: The **Enter** key is the accelerator key for this action.

2.2.10 Cycle Options



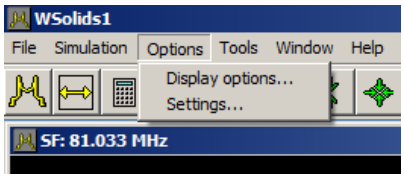
The item **Cycle options** of the Simulation (p. 28) popup menu allows to customize the detailed course of the Cycle (p. 38) feature. This cycle consists of:

Selection	Action
Windows	After all other cycle steps were performed for a window, switch to the next spectrum window

Default parameters	Edit the spectrum default parameters for the currently active spectrum window
Site parameters	Edit the site-specific parameters for each available site
Convolution parameters	Edit the convolution parameters
Calculation	Perform calculation of a theoretical spectrum and display the result

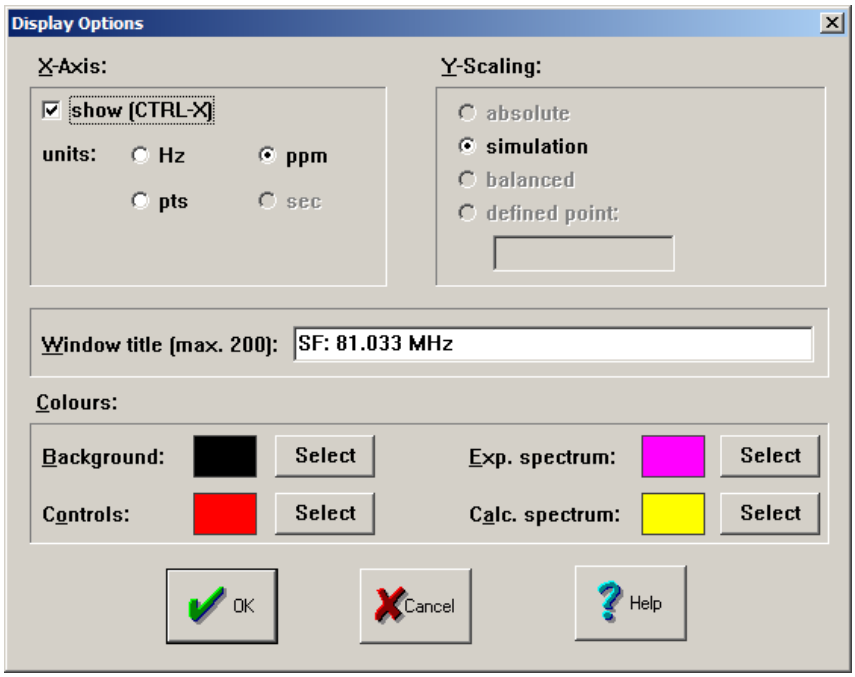
2.3 Options Menu

The Options pop-up menu consists of the following items:



Item	Purpose
Display Options (p. 39)	Invokes a dialog box with parameters that determine the properties of the spectrum window
Settings (p. 40)	Invokes a dialog box with some program settings

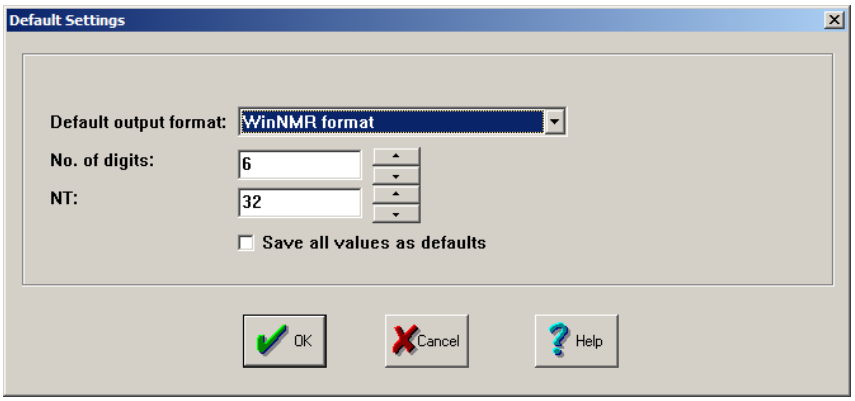
2.3.1 Display Options



This dialog contains parameters to adjust the spectrum window properties:

- **X-Axis**: this group allows to switch between the X axis units displayed underneath the spectra: Hz, ppm, points (sec is only available for FIDs)
- **Y-Scaling**: right now only one option: simulation
- **Window title**: some text to identify the spectrum window; the default settings is to display SF (p. 29)
- the colours of several spectrum items

2.3.2 Settings

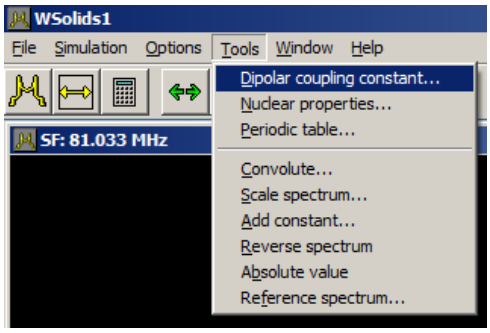


This dialog allows to modify, either temporarily or permanently, some program settings that are retrieved from the ini file (p. 97) upon program start:

- **Default output format**: the default output format (p. 98) for saving spectra (p. 22)
- **no. of digits**: the number of decimal digits (p. 99) to be displayed in edit controls
- **NT**: the number of triangular intersections (p. 98)
- **Save values as default**: if checked, the changes will be saved in the INI file (p. 97), otherwise they affect the program only temporarily.

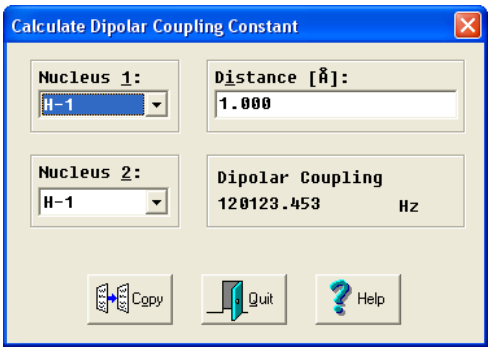
2.4 Tools Menu

The Tools pop-up menu consists of the following items:



Item	Purpose
Dipolar coupling constant (p. 41)	Invokes a dialog box to calculate dipolar coupling constants
Nuclear properties (p. 42)	Displays a table of nuclear properties
Periodic table (p. 44)	Displays a periodic system of elements relevant to NMR
Convolute (p. 44)	Performs an additional convolution of experimental or theoretical spectra
Scale spectrum (p. 44)	Scale a spectrum by a given factor
Add constant (p. 45)	Adds the specified value to the intensity of the spectrum
Reverse spectrum (p. 45)	Reverses the frequency direction of the spectrum
Absolute value (p. 45)	Generates the absolute-value representation of the spectrum
Reference spectrum (p. 45)	Add a shift to the experimental or calculated spectrum

2.4.1 Dipolar Coupling Constant



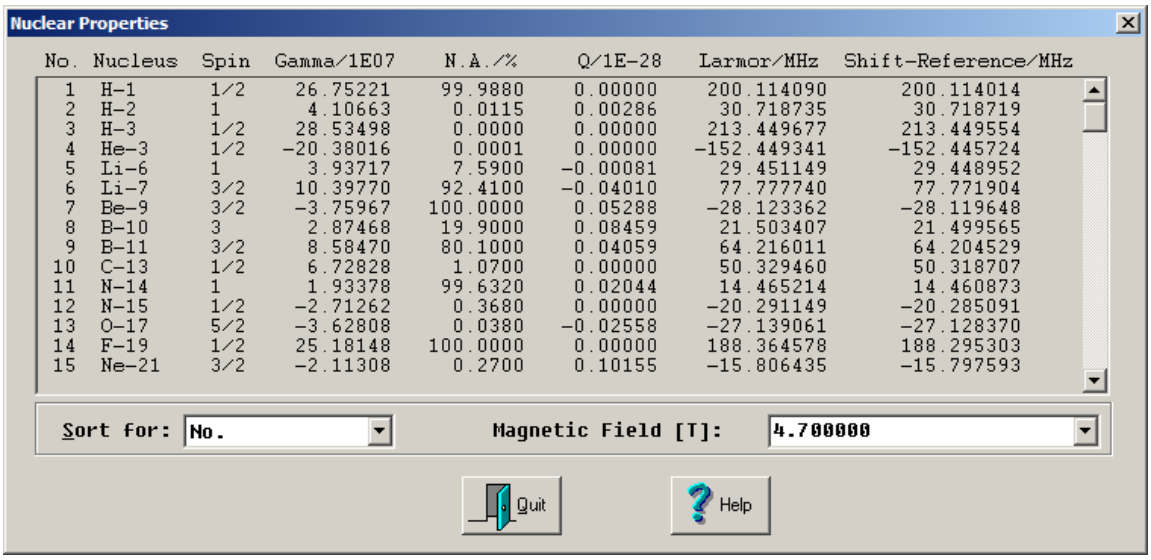
Selection of the **Tools**|**Dipolar coupling constant** menu item invokes this dialog box.

To calculate the dipolar coupling constant, follow these steps:

- Select from the two list boxes **Nucleus 1** and **Nucleus 2** the two nuclei constituting the spin pair (use mouse, arrow keys, or first letter of nucleus).
- Enter the internuclear separation in Angstrom.
- Hit **Enter** to display the calculated dipolar coupling constant
- If required, copy the result to the clipboard by pushing the **Copy** button (or ALT-O). This can be used to **paste** (typically CTRL-V or SHIFT-INSERT) the result into appropriate edit controls
- Exit the dialog by selecting **Quit** (or ESC)

For information on the source of the nuclear data, refer to Table of Nuclear Properties (p. 42).

2.4.2 Table of Nuclear Properties



No.	Nucleus	Spin	Gamma/1E07	N.A./%	Q/1E-28	Larmor/MHz	Shift-Reference/MHz
1	H-1	1/2	26.75221	99.9880	0.00000	200.114090	200.114014
2	H-2	1	4.10663	0.0115	0.00286	30.718735	30.718719
3	H-3	1/2	28.53498	0.0000	0.00000	213.449677	213.449554
4	He-3	1/2	-20.38016	0.0001	0.00000	-152.449341	-152.445724
5	Li-6	1	3.93717	7.5900	-0.00081	29.451149	29.448952
6	Li-7	3/2	10.39770	92.4100	-0.04010	77.777740	77.771904
7	Be-9	3/2	-3.75967	100.0000	0.05288	-28.123362	-28.119648
8	B-10	3	2.87468	19.9000	0.08459	21.503407	21.499565
9	B-11	3/2	8.58470	80.1000	0.04059	64.216011	64.204529
10	C-13	1/2	6.72828	1.0700	0.00000	50.329460	50.318707
11	N-14	1	1.93378	99.6320	0.02044	14.465214	14.460873
12	N-15	1/2	-2.71262	0.3680	0.00000	-20.291149	-20.285091
13	O-17	5/2	-3.62808	0.0380	-0.02558	-27.139061	-27.128370
14	F-19	1/2	25.18148	100.0000	0.00000	188.364578	188.295303
15	Ne-21	3/2	-2.11308	0.2700	0.10155	-15.806435	-15.797593

This dialog box, accessible from the **Tools**|**Nuclear properties** menu item, lists nuclear properties for many of the known NMR active nuclei:

The Properties:

- nuclear **spin** quantum number
- magnetogyric ratio γ, **Gamma**, in units of 10^7 rad s^{-1} T^{-1}
- natural abundance, **N.A.**, in %
- nuclear electric quadrupole moment, **Q**, in units of 10^{-28} m^2
- Larmor frequency, in MHz, of that nucleus at the selected magnetic field strength, according to

$$\nu_L = \frac{\gamma}{2\pi} B_0$$

- frequency, in MHz, of the reference compound for that nucleus (i.e., chemical shift reference, secondary standard) at the selected magnetic field strength, according to

$$\nu = \Xi \quad \frac{B_0}{2.348661}$$

using the absolute frequency ratio Ξ as defined by IUPAC [6].

Sorting:

By default, the nuclei are listed according to their position in the periodic table of elements (i.e. for increasing mass number). Using the **Sort for:** list box, the display can be sorted alphabetically for the labels of the nuclei, the spin, the magnetogyric ratio (Gamma), the natural abundance, or the nuclear electric quadrupole moment.

Magnetic Field:

The strength of the magnetic field, affects the frequency of the reference compound. The following values produce the given values of the ^{1}H NMR frequency of TMS:

B_0 / T	^{1}H frequency of TMS / MHz
2.348661	100.00
4.700374	200.13
5.874703	250.13
7.049034	300.13
9.397695	400.13
11.746354	500.13
14.0950140	600.13
16.443674	700.13
18.792334	800.13
21.140994071	900.13
22.3153239	950.13

Copying Data:

Note that it is possible to high-light parts of the table and to copy the highlighted parts to the clip-board using standard Windows editing techniques (CTRL-INSERT or CTRL-C to copy the selected part).

Modifications:

Most nuclear data have originated from Mason's extremely useful book on *Multinuclear NMR* [1]. The current version of R has been updated according to data from the *IUPAC Recommendations 2001* [6]. The following data differ from those in reference [1], all magnetogyric ratios are according to [6]:

- the nuclear quadrupole moment values are from the "Year 2001 Q Values" collected by Pekka Pyykkö [3];
- the magnetogyric ratios of Sn-119 and Sn-117 could be 3 % less than the accepted value [2], i.e., 9.997559×10^7 rad s^{-1} T^{-1} and 9.552955×10^7 rad s^{-1} T^{-1} instead of 10.021×10^7 rad s^{-1} T^{-1} and 9.589×10^7 rad s^{-1} T^{-1}.
- Nd-145 apparently has a spin of 7/2 instead of 5/2 [4,5]. Similarly, U-235 has a spin of 7/2 instead of 5/2 [4,5]. U-233 has been added to the tables [4,5].

References:

(1) Joan Mason, *Multinuclear NMR*, Plenum Press, New York, 1987.

(2) A. Laaksonen and R. Wasylishen, *J. Am. Chem. Soc.* **1995**, *117*, 392−400, DOI: 10.1021/ja00106a044.

(3) P. Pyykkö, *Mol. Phys.* **2001**, *99*, 1617−1629, DOI: 10.1080/00268970110069010.

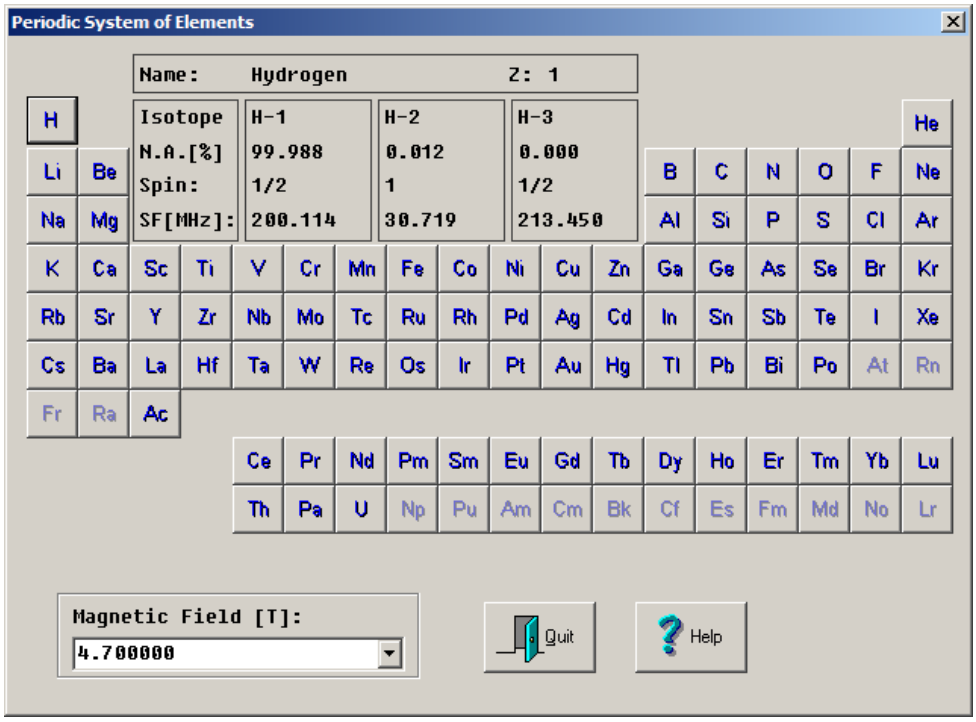
(4) *Quantities, Units and Symbols in Physical Chemistry (IUPAC)*

(5) *CRC Handbook of Chemistry and Physics*

(6) R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger:

– *Pure Appl. Chem.* **2001**, *73*, 1795-1818, DOI: 10.1351/pac200173111795.
– *Solid State Nucl. Magn. Reson.* **2002**, *22*, 458−483, DOI: 10.1006/snmr.2002.0063.
– *Angew. Chem.* **2004**, *116*, 2070-2083, DOI: 10.1002/ange.200380015.

2.4.3 Periodic System of Elements



This dialog box, accessible from the **Tools**|**Periodic table** menu item, displays a periodic system of elements with information relevant to NMR.

By setting the magnetic field induction strength, B_0, to a specific value in Tesla, this dialog box calculates the corresponding frequency of the reference compound for the isotopes of the selected element. The default value causes the H-1 peak of TMS to have a resonance frequency of 100.00 MHz.

The default value of the magnetic field is retrieved from the INI file and can be changed there. If there is no INI file or no corresponding entry in the INI file, the default value is 2.348661 T.

For information on the source of the nuclear data, refer to Table of Nuclear Properties (p. 42).

2.4.4 Convolute

This option, available from the **Tools**|**Convolute** menu, enables one to apply additional Convolution (p. 32) to experimental or calculated spectra.

For example, if a calculation takes a long time, it is advisable not to include any convolution into the calculation itself, but to save the calculated spectrum to a file and apply convolution separately afterwards.

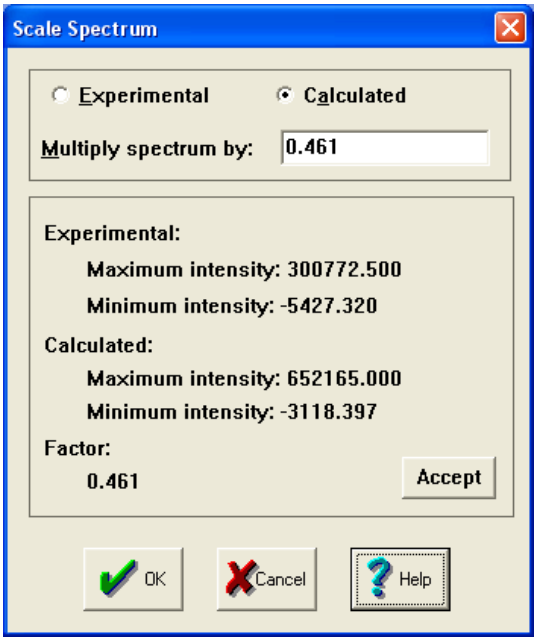
2.4.5 Scale Spectrum

This option, available from the **Tools**|**Scale spectrum** menu, enables one to multiply a specific spectrum by a given factor.

For example, if one exports a spectrum from WinNMR as ASCII file, the spectrum may look "jagged", because WinNMR converts the intensities into integers and the spectrum did not take advantage of

the full dynamic range. This "digitization" loss can be circumvented by scaling the intensities up by some factor.

Also, when saving spectra (p. 22) in TopSpin format, it is advisable to scale up the calculated spectrum. The dialog displays the minimum and maximum intensities of the available spectra and suggests a scaling factor. If you agree with the suggested factor, press the **Accept** button to update the value in the field **Multiply spectrum by**. After hitting the **OK** button, the selected spectrum will be multiplied by this value. The **Cancel** button quits this dialog without performing any changes.



2.4.6 Add Constant

This option, available from the **Tools**|**Add constant** menu, enables one to add a constant value to an existing spectrum, basically a constant base line correction.

2.4.7 Reverse Spectrum

This option, available from the **Tools**|**Reverse spectrum** menu, enables one to reverse the frequency direction of the spectrum.

Physically, for a spectrum consisting of n points, this exchanges the intensity of the first and n-th point, the second and (n-1)-th point, and so on. Some versions of WinNMR do not provide such a functionality to swap the high- and low-frequency halves of the spectrum, although some Bruker spectrometers produce(d) spectra for which this is (was) necessary.

2.4.8 Absolute Value

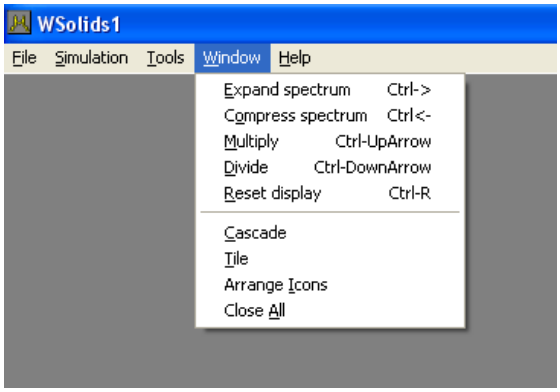
This option, available from the **Tools**|**Absolute value** menu, enables one to generate the absolute value representation of the spectrum.

2.4.9 Reference Spectrum

This feature, available from the **Tools**|**Reference spectrum** menu, is not intended to be some fancy referencing tool, but to shift the experimental or calculated spectrum by adding a specified shift to the spectrum. Such a feature could be helpful when simulating simultaneously spectra at different magnetic fields or different spinning angles and small adjustments in referencing are necessary.

2.5 Window Menu

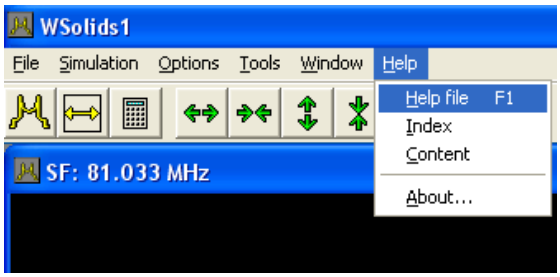
The Window menu allows management of spectrum windows and select display regions. It consists of the following items:



Item	Action
Expand spectrum	Horizontally expand spectra (frequency scale) in the currently active spectrum window
Compress spectrum	Horizontally contract spectra (frequency scale) in the currently active spectrum window
Multiply	Scale up the intensities of spectra in the currently active spectrum window
Divide	Scale down the intensities of spectra in the currently active spectrum window
Reset display	Resets the display limits such that the spectra are fully visible
Cascade	Cascade all open spectrum windows
Tile	Arrange all open spectrum windows so that each has the same area
Arrange Icons	Arrange the icons of minimized spectrum windows
Close All	Close all spectrum windows

2.6 Help Menu

The Help menu allows access to a variety of information. It consists of the following items:



Item	Action
Help file	Opens the WSolids1 help file on its front page
Index	Opens the WSolids1 help file at its index page
Content	Opens the WSolids1 help file at its table of contents page
About	Displays information about the current version and build number of WSolids1.

Initially, WSolids1 used for help and documentation the Windows Help program. Since version 1.19.4 I switched to the PDF format because it is suitable for both online viewing as well as printing. To view or print this documentation, any PDF viewer should work. Also, most viewers should be able to deal with the hyperlinks that cross-link topics in this help file. However, opening a PDF file at a specified position is more complicated. Therefore, not every PDF viewer will work with WSolids1 to display context sensitive help. This matter is aggravated by the fact that every viewer has its own mechanism!

Currently, context sensitive help should work with the following PDF viewers:

- Adobe uses with its `Acrobat Reader` series of products a mechanism called Dynamic Data Exchange (DDE) to open a PDF file at a specific position. For ages, the name of the DDE server has been `acroview`. However, with the introduction of Acrobat Reader X this tradition has been broken on purpose, breaking many applications that rely on this mechanism. WSolids1 should be able to work with older versions of the Acrobat Reader as well as with the `acroviewR10` DDE server of Adobe Reader X. Because I have been quite dissatisfied with the Adobe products from Reader 5 onwards, I am using a different PDF viewer and will not always check whether Acrobat is still working.
- My prefered PDF viewer is the free `PDF XChange Editor`, the successor of `PDF XChange Viewer` by Tracker Software Products, Ltd. (`http://www.tracker-software.com`), more powerful and reliable than the Acrobat Reader. The opening of a PDF file at a specific position is achieved via command line parameters.
- Another viewer used by people working with LaTeX is the `Sumatra PDF Viewer` (`http://blog.kowalczyk.info/software/sumatrapdf`), also supported by WSolids1.
- Other PDF viewers such as FoxIt or NitroPDF do not support DDE or command line parameters, as far as I know.

2.7 Known Problems

Usually, I will try to keep the content of this page as small as possible ;-)

- There is a problem in the MAS: Spin-1/2 – Spin-S (Diag.) (p. 67) model when the observed nucleus has a negative magnetogyric ratio. In these cases it might appear that the quadrupolar coupling constant has the opposite sign. There is no quick fix right now; contact me if you need more information.

3 Spin Systems

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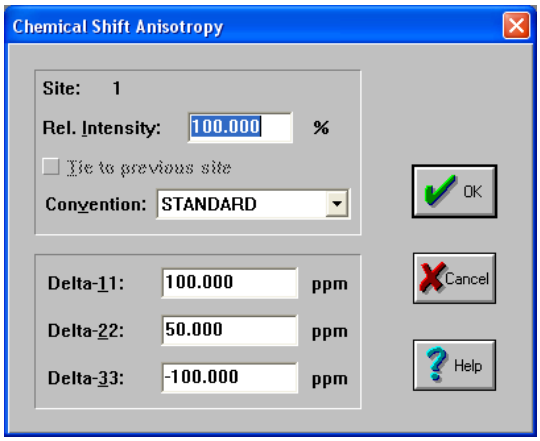
3.1 Static: Chemical Shift Anisotropy



This model calculates the spectrum of a static powder sample showing only chemical shift anisotropy ("powder pattern").

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Convention (p. 88)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 88)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 88)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 88)	Principal components of chemical shift tensor (Haeberlen convention)
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

Depending on the local symmetry at the nuclear site, the magnitude of the chemical shift will vary as a function of the orientation of the molecule with respect to the external magnetic field. This orientation dependence of the chemical shift is referred to as chemical shift anisotropy (CSA). Mathematically, the chemical shift anisotropy is described by a second-rank tensor (a 3 by 3 matrix), which in the case of the symmetric part of the chemical shift (CS) tensor consists of six independent components. Generally, one is able to express the chemical shift tensor in a coordinate frame where all off-diagonal elements vanish. In this principal axis system, the chemical shift tensor is fully described by the three diagonal elements, the principal components, and the three eigenvectors or Euler angles describing the orientation of the principal axes with respect to an arbitrary frame.

Due to the chemical shift anisotropy, the spectrum of a static powder sample, where statistically all

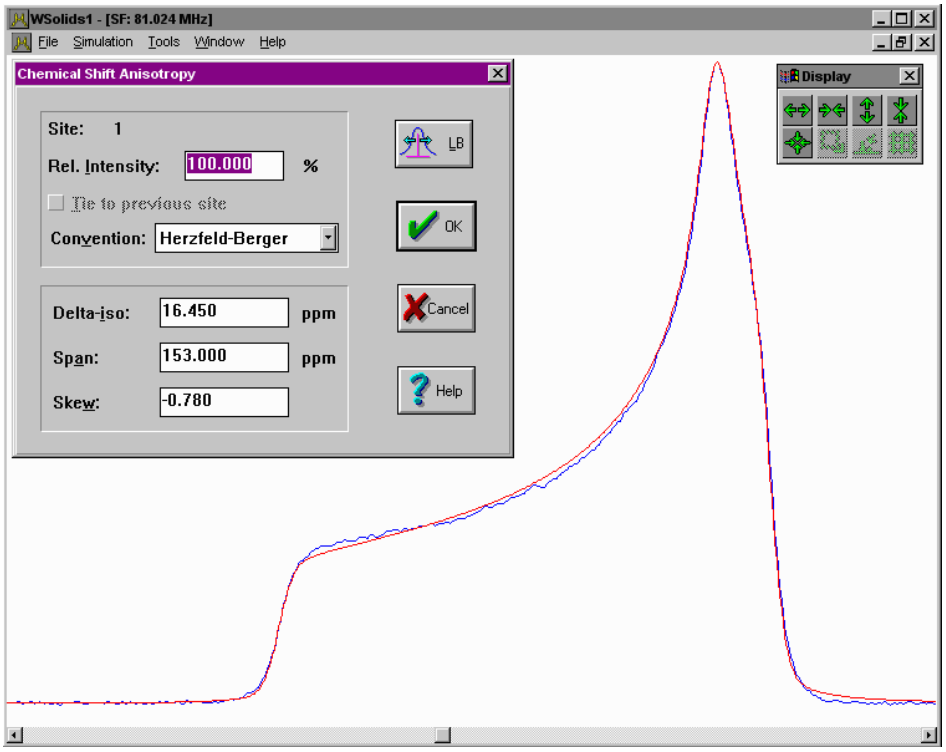


Figure 3.1: Experimental and calculated ^{31}P NMR spectra of a static powder sample of a molybdenum phosphine complex.

orientations of the molecule with respect to the magnetic field are present, will consist of a broad line shape with three distinct features, corresponding to the principal components. However, note that for a powder sample there is generally no information about the orientation of the principal components in the molecular frame of reference. Exceptions are cases where crystallographic or local symmetry put restrictions on the orientation, or if a second interaction, e.g., the dipolar interaction (see Static: Dipolar Chemical Shift (A2, AX) (p. 52)).

Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

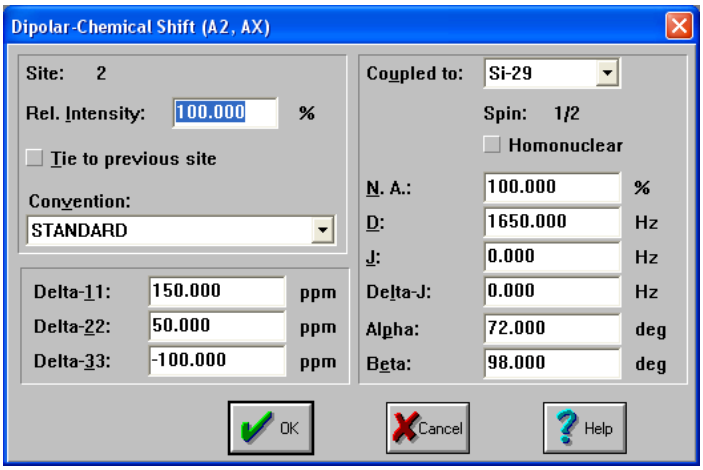
K. Eichele, R. E. Wasylishen, *J. Magn. Reson. A* **106** (1994) 46−56, DOI: 10.1006/jmra.1994.1005.

This model employs the POWDER space tiling and interpolation procedure.

Figure 3.1 shows an example of the succesful simulation of a spectrum arising from the chemical shift anisotropy of a powder sample. It is the ^{31}P NMR spectrum of a molybdenum phosphine complex and the results have been published in:

Single-Crystal ^{31}P NMR and X-ray Diffraction Study of a Molybdenum Phosphine Complex: (5-Methyldibenzophosphole)pentacarbonylmolybdenum(0).
K. Eichele, R.E. Wasylishen, K. Maitra, J.H. Nelson, J.F. Britten, *Inorg. Chem.* **1997**, *36*, 3539-3544, DOI: 10.1021/jp9712415.

3.2 Static: Dipolar Chemical Shift (A2, AX)



Calculates the spectrum of a static powder sample containing an isolated spin pair considering chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling. The spin pair can be a homonuclear pair of magnetically equivalent spin-1/2 nuclei or a heteronuclear pair (A2 or AX approximation). It is assumed that the dipolar interaction and the anisotropy are both collinear and axially symmetric.

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Convention (p. 88)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 88)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 88)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 88)	Principal components of chemical shift tensor (Haeberlen convention)
Coupled to (p. 91)	Specifies the nucleus the observed nucleus is coupled to. If this is the same isotope as the observed nucleus, the checkbox **homonuclear** becomes checked
N.A. (p. 91)	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
D (p. 91)	Direct dipole-dipole coupling constant, in Hz
J (p. 92)	Indirect spin−spin coupling constant, in Hz
Delta-J (p. 92)	Anisotropy of the indirect spin-spin coupling, in Hz

Alpha (p. 92)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
Beta (p. 92)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation.

For historical reasons, this model works slightly different from the other models. Via the parameters relative intensity and natural abundance, one can calculate coupled and uncoupled spectra directly, without defining a separate spin system for each. This is ok for spin systems where the observed nucleus is coupled to an NMR active isotope and an NMR passive isotope. However, to deal with situations where the observed nucleus is coupled to an NMR passive isotope and several different NMR active isotopes, the generation of several spin systems is required.

Example: P-31 coupled to cadmium (Cd-111: 12.75%, Cd-113: 12.26%, passive: 74.99%).

- One could use three different sites, with the relative intensity reflecting the natural abundancies of each isotope (and tying the parameters of the sites together), while the natural abundance parameter is set to 100% (except for the passive site, where this parameter should be zero).
- Or, one could use two different sites. The first site should correspond to coupling with one of the active cadmium isotopes, say Cd-111 (rel. intensity: 12.75%, nat. abund.: 100%). The second site reflects both coupling to Cd-113 as well as the passive cadmium, thus rel. intensity = 87.25%, nat. abund. = 14.05% — because 14.05% of 87.25% corresponds to 12.26% in total)

Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

K. Eichele, R. E. Wasylishen, *J. Magn. Reson. A* **106** (1994) 46-56, DOI: 10.1006/jmra.1994.1005.

Furthermore, this article describes the technique of analyzing spectra using the dipolar-splitting-ratio method and outlines the background behind the program DSR.

This model employs the POWDER space tiling and interpolation procedure.

Figure 3.2 shows an example of the succesful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear dipolar coupling in a powder sample. It is the ^{31}P NMR spectrum of tetraethyl diphosphine disulfide, shown as absorption and first derivative spectrum, and the results have been published in:

Phosphorus-31 NMR Studies of Solid Tetraethyldiphosphine Disulfide. A Reinvestigation of the $^{31}P,^{31}P$ Spin-Spin Coupling Tensor.
K. Eichele, G. Wu, R. E. Wasylishen, J. F. Britten, *J. Phys. Chem.* **1995**, *99*, 1030-1037, DOI: 10.1021/j100003a028.

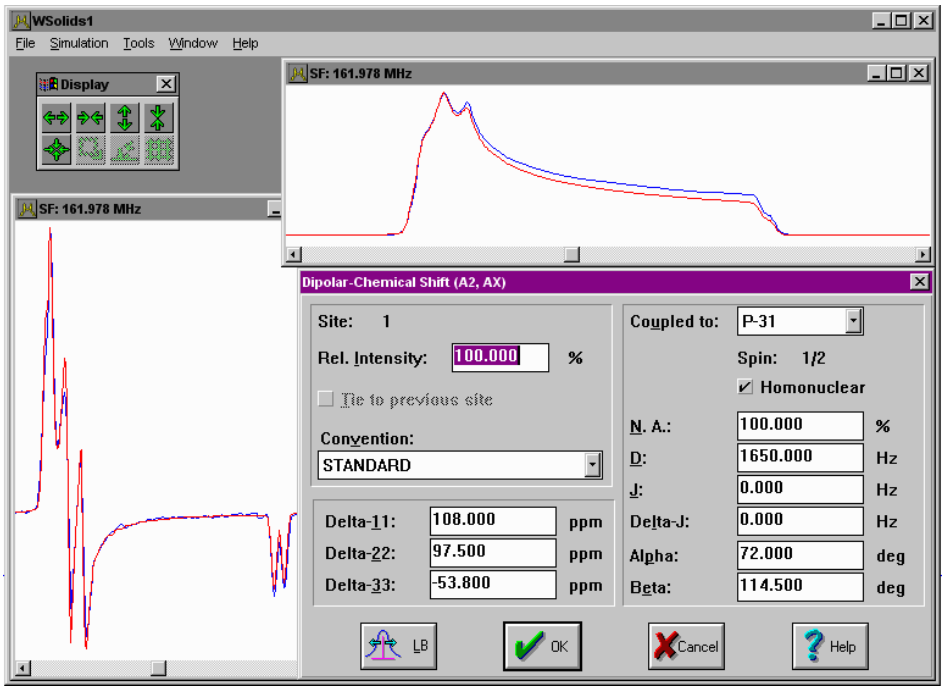
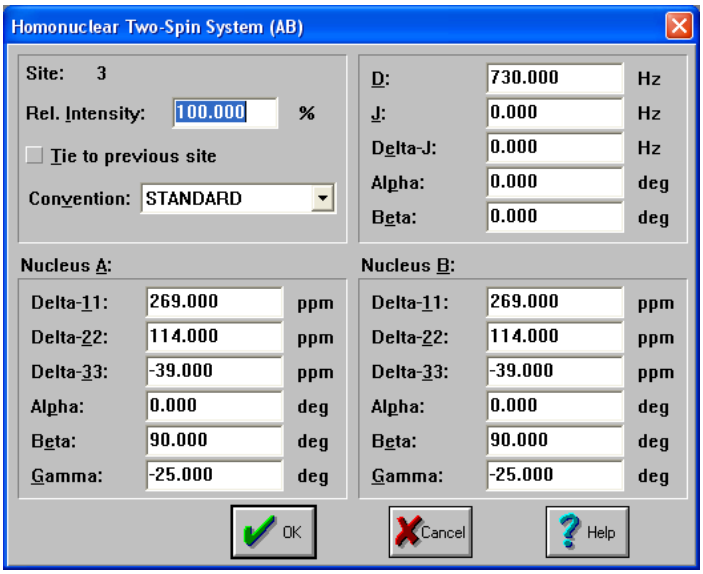


Figure 3.2: Experimental and calculated ^{31}P NMR spectra of a static powder sample of tetraethyl diphosphine disulfide.

3.3 Static: Dipolar Chemical Shift (AB)



Calculates the spectrum of a static powder sample containing an isolated spin pair of homonuclear spin-1/2 nuclei, considering chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling, including second order effects. It is assumed that the dipolar and indirect coupling tensors are colinear and axially symmetric.

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Convention (p. 88)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 88)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 88)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 88)	Principal components of chemical shift tensor (Haeberlen convention)
Alpha, Beta, Gamma (p. 93)	Euler angles, in degrees, for going from the crystal frame to the principal axis system of the chemical shift tensors
D (p. 91)	Direct dipole-dipole coupling constant, in Hz
J (p. 92)	Indirect spin−spin coupling constant, in Hz
Delta-J (p. 92)	Anisotropy of the indirect spin-spin coupling, in Hz
Alpha (p. 92)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor

Beta (p. 92)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. In contrast to the A_2 and AX first-order spin systems, the line shape of a general homonuclear AB spin system may also depend on the relative orientations of the two chemical shift tensors.

Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

K. Eichele, R. E. Wasylishen, *J. Magn. Reson. A* **106** (1994) 46-56, DOI: 10.1006/jmra.1994.1005.

This model employs the POWDER space tiling and interpolation procedure.

Figure 3.3 shows an example of the succesful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear dipolar coupling in a powder sample. It is the 31P NMR spectrum of pentacarbonyl molybdenum [bis(diphenylphosphino) methane], shown as absorption and first derivative spectrum, and the results have been published in:

Phosphorus-31 Solid-State NMR Studies of Homonuclear Spin Pairs in Molybdenum Phosphine Complexes: Single-Crystal, Dipolar-Chemical Shift, Rotational-Resonance and 2D Spin-Echo NMR Experiments
K. Eichele, G. Ossenkamp, R. E. Wasylishen, T. S. Cameron, J. F. Britten, *Inorg. Chem.* **1999**, *38*, 639-651, DOI: 10.1021/ic9806232.

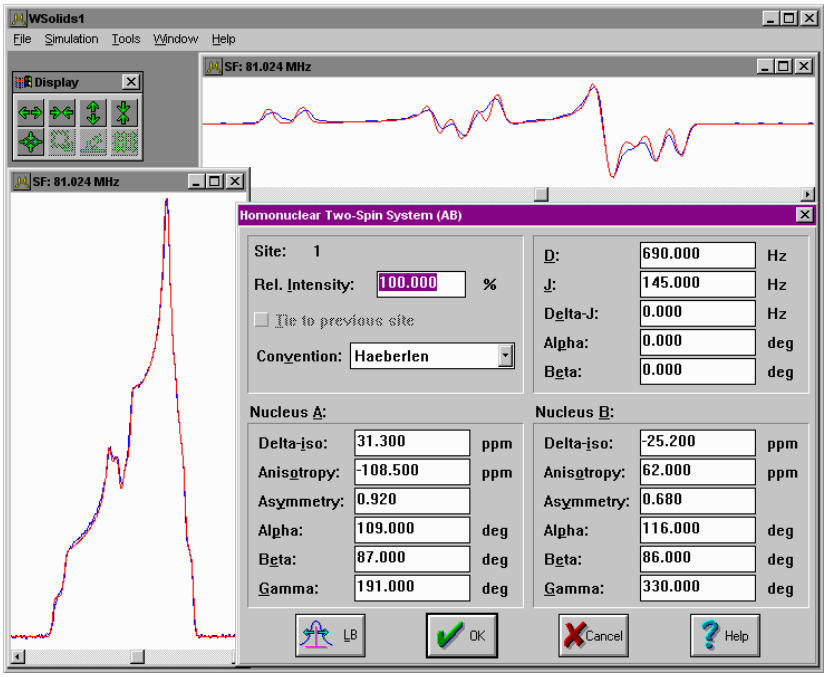
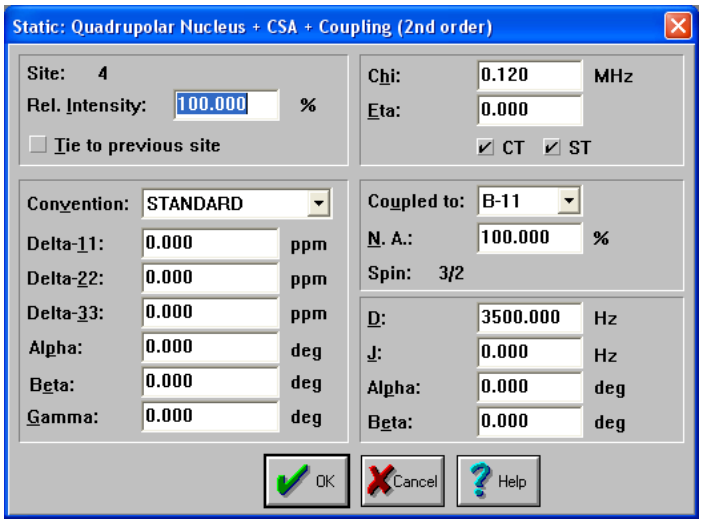


Figure 3.3: Experimental and calculated ^{31}P NMR spectra of a static powder sample of $Mo(CO)_5$(dppm).

3.4 Static: Quadrupolar Nucleus



Calculates the static powder spectrum of a quadrupolar nucleus, considering the quadrupolar interaction up to second order. Additionally, chemical shift anisotropy, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Convention (p. 88)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 88)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 88)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 88)	Principal components of chemical shift tensor (Haeberlen convention)
Alpha, Beta, Gamma (p. 93)	Euler angles, in degrees, for going from the electric field gradient tensor frame to the principal axis system of the chemical shift tensor
Chi (p. 96)	Quadrupolar coupling constant, in MHz
Eta (p. 96)	Asymmetry parameter of the electric field gradient tensor, 0 <= eta <= 1
CT,ST (p. 96)	Select central transition (CT) or satellite transitions (ST)

Coupled to (p. 91)	Specifies the nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
N.A (p. 91)	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
D (p. 91)	Direct dipole-dipole coupling constant, in Hz
J (p. 92)	Indirect spin−spin coupling constant, in Hz
Delta-J (p. 92)	Anisotropy of the indirect spin-spin coupling, in Hz
Alpha (p. 92)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
Beta (p. 92)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a quadrupolar nucleus will also depend on the nuclear quadrupolar interaction and the relative orientation of both interactions. The quadrupolar interaction is considered up to second order for the observed nucleus. Optionally, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Implementation Details

Specifically, we use the following conventions:

- the NQR notation is used for labelling the axes of the EFG tensor: $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$
- the orientation of the field is given by the polar angle beta (wrt. V_{ZZ}) and the azimuth alpha, the angle between the projection of B_0 into the $V_{XX} - V_{YY}$ plane and V_{XX} (cf. Abragam)
- direction cosines of the shielding tensor with respect to the EFG frame are obtained via the Euler angles following Arfken's convention, with the initial alignment 11-XX, 22-YY, 33-ZZ

Figure 3.4 shows an example for the successful simulation of a spectrum of a quadrupolar nucleus that shows the combined effect of chemical shift anisotropy and quadrupolar interaction in a powder sample. It is the ^{133}Cs NMR spectrum of cesium cadmium thiocyanate, $CsCd(SCN)_3$, and the results have been published in:

Cesium-133 NMR Study of $CsCd(SCN)_3$: Relative Orientation of the Chemical Shift and Electric Field Gradient Tensors.
S. Kroeker, K. Eichele, R.E. Wasylishen, J.F. Britten, *J. Phys. Chem. B* **1997**, *101*, 3727-3733, DOI: 10.1021/jp970043a.

References

(1) The first-order expression is taken from Amoureux's treatment, which follows Abragam and Taulelle:
Amoureux, Fernandez, Granger, In *Multinuclear Magnetic Resonance in Liquids and Solids - Chemical Applications*; Granger, Harris, eds.; Kluwer Academic Publishers, 1990; Ch. 22, p 409

(2) The second-order expression is taken from:
G. H. Stauss, *J. Chem. Phys.* **1964**, *40*, 1988, DOI: 10.1063/1.1725432.

(3) Related papers:
K. Narita, J.-I. Umeda, H. Kusumoto, *J. Chem. Phys.* **1966**, *44*, 2719, DOI: 10.1063/1.1727118.
J. F. Baugher, P. C. Taylor, T. Oja, P. J. Bray, *J. Chem. Phys.* **1969**, *50*, 4914, DOI: 10.1063/1.1670988.

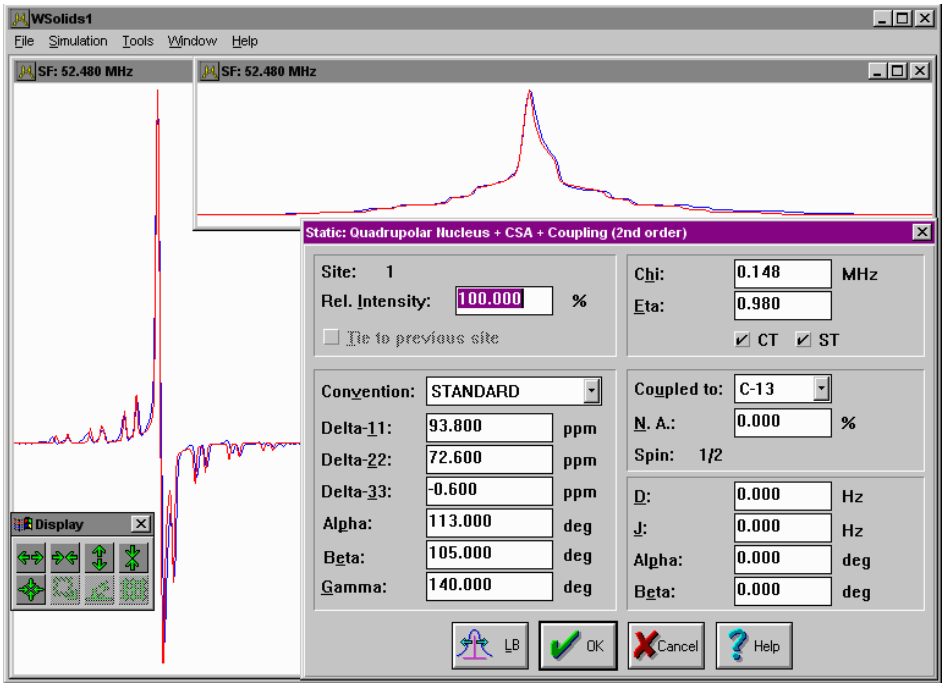
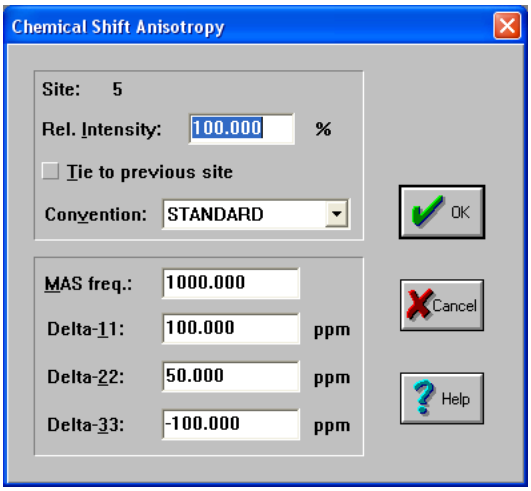


Figure 3.4: Experimental and calculated ^{133}Cs NMR spectra of a static powder sample of cesium cadmium thiocyanate.

3.5 Static: Three-Spin System (AMX)

this calculation has not been verified yet, use at your own risk!

3.6 MAS: Chemical Shift Anisotropy (HB)



This model calculates the spectrum of a powder sample spinning at the magic angle showing chemical shift anisotropy only.

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
MAS freq. (p. 97)	Spinning frequency in Hz
Convention (p. 88)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 88)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 88)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 88)	Principal components of chemical shift tensor (Haeberlen convention)
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin in a powder sample under-magic angle spinning will depend on the spinning frequency, if the spinning frequency is lower than the width of the chemical shift powder pattern. In this case, the isotropic peak (center peak) is flanked by spinning sidebands spaced at integer multiples of the spinning frequency. The intensities of the spinning sidebands are intimately related to the principal components of the chemical shift tensor.

For efficiency reasons, WSolids1 uses look-up tables of precomputed spinning sideband intensities,

according to the method of Herzfeld-Berger (HB). The tables used by WSolids1 have been extended compared to the original Herzfeld-Berger publication, from $\mu = 15$ to $\mu = 30$, and includes ± 15 spinning sidedands instead of ± 5 (for the definition of μ, see Herzfeld-Berger Convention (p. 89)). Roughly, μ corresponds to the number of significant spinning sidebands visible in the spectrum. The current extent of the Herzfeld-Berger tables is often good enough for the analysis of spinning sideband intensities to retrieve chemical shift tensor components (see my program HBA), but for great values of μ some spinning sidebands might be missing in a simulation. Therefore, WSolids1 uses a different approach to calculate spinning sideband intensities if μ exceeds a certain limit, 20 currently. The calculation is done in the frequency domain as outlined in the Herzfeld-Berger paper, each spinning sideband is calculated individually. More information will be available in the section VAS: Dipolar-Chemical Shift (A2,AX) (p. 76). If the angle of the spinning axis deviates from the magic angle, you should use that model to simulate pure chemical shift anisotropy cases, despite the name of the model indicating spin pairs.

Figure 3.5 shows an example for the succesful simulation of a spectrum arising from chemical shift anisotropy in a powder sample under magic-angle spinning. It is the ^{31}P CP/MAS NMR spectrum of a phosphinidene ruthenium cluster, *nido*-$Ru_4(CO)_{13}(\mu_3$-PPh), and the results have been published in:

Phosphorus-31 Chemical Shift Tensors of Phosphinidene Ligands in Ruthenium Carbonyl Cluster Compounds: A ^{31}P Single-Crystal and CP/MAS NMR Study.
K. Eichele, R. E. Wasylishen, J. F. Corrigan, N. J. Taylor, A. J. Carty, *J. Am. Chem. Soc.* **1995**, *117*, 6961-6969, DOI: 10.1021/ja00131a019.

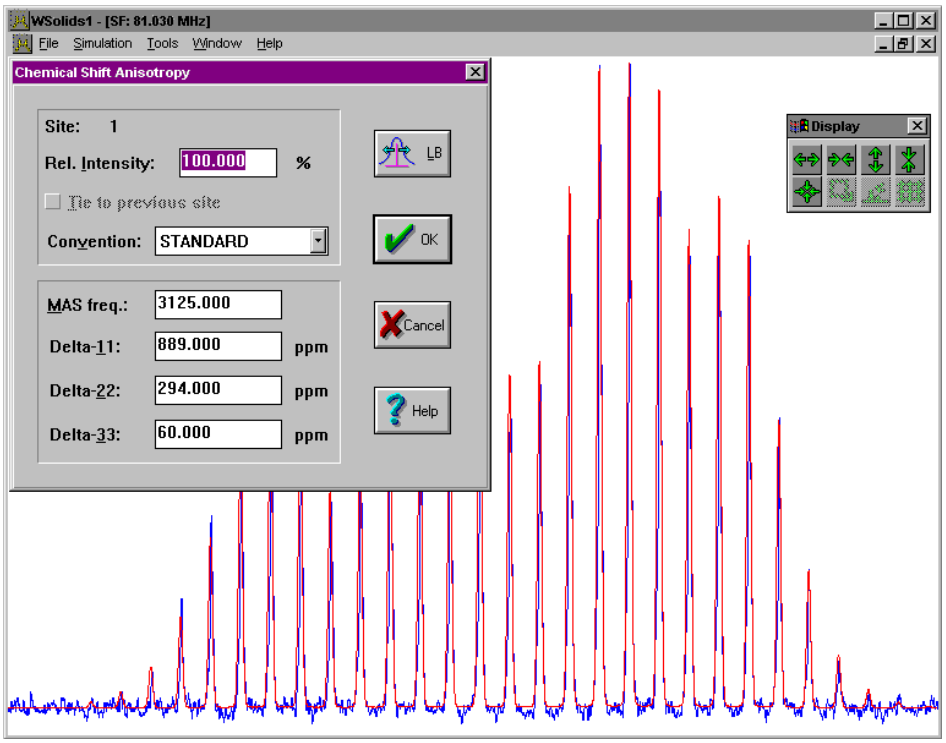
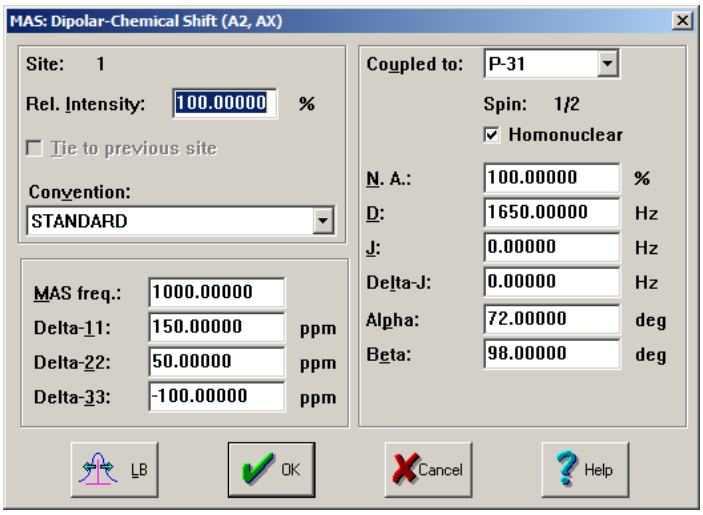


Figure 3.5: Experimental and calculated ^{31}P MAS NMR spectra of a powder sample of a phosphinidene ruthenium cluster.

3.7 MAS: Dipolar-Chemical Shift (A2, AX)



Calculates the spectrum of a powder sample containing an isolated spin pair and spinning at the magic angle, considering chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling. The spin pair can be a homonuclear pair of magnetically equivalent spin-1/2 nuclei or a heteronuclear pair (A2 or AX approximation). It is assumed that the dipolar interaction and the anisotropy are both collinear and axially symmetric.

This model uses the same parameters as the Static Dipolar Chemical Shift (A2, AX) (p. 52) model. In addition, the parameter MAS freq. (p. 97) as spinning frequency in Hz is required.

Similar to the MAS: Chemical Shift Anisotropy (HB) (p. 62) model, this model uses Herzfeld-Berger tables to look up spinning sideband intensities, if the range of these tables allows so (see MAS: Chemical Shift Anisotropy (HB) (p. 62) for more details).

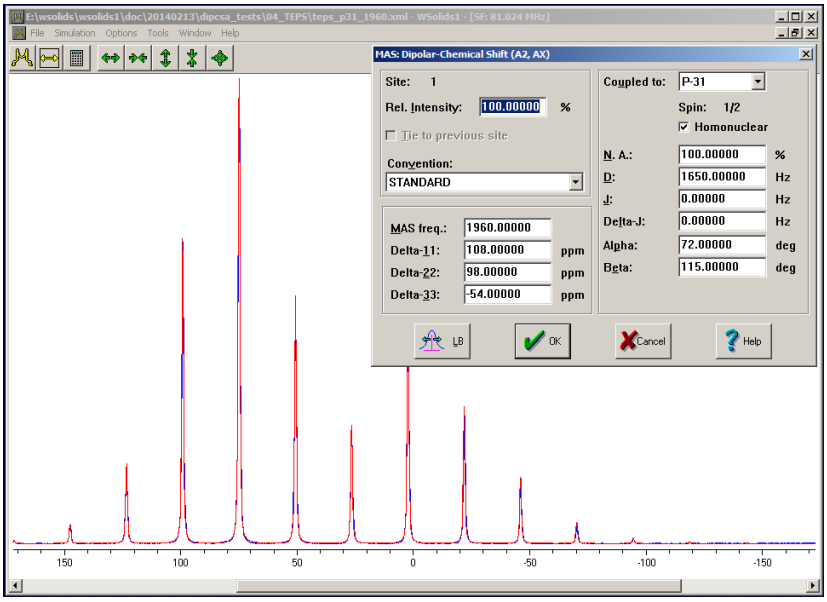
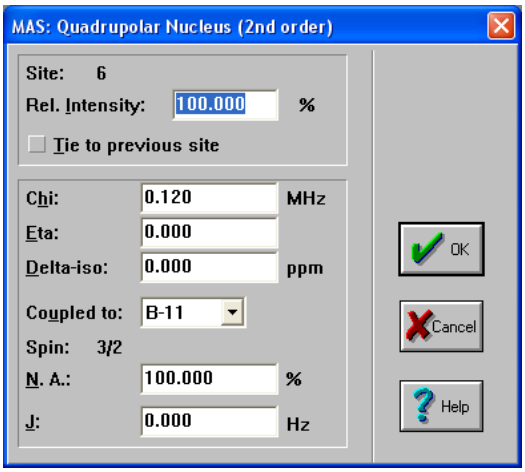


Figure 3.6: Experimental and calculated ^{31}P MAS NMR spectra of a powder sample of tetraethyl diphosphine disulfide (TEPS).

3.8 MAS: Quadrupolar Nucleus



Calculates powder MAS spectrum of the central transition of a quadrupolar nucleus, considering the quadrupolar interaction to second order. Additionally, indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Delta-iso (p. 88)	Isotropic chemical shift, in ppm
Chi (p. 96)	Quadrupolar coupling constant, in MHz
Eta (p. 96)	Asymmetry parameter of the electric field gradient tensor, 0 <= eta <= 1
Coupled to (p. 91)	Specifies the nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
N.A (p. 91)	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
J (p. 92)	Indirect spin−spin coupling constant, in Hz
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

If the nuclear quadrupolar coupling for a quadrupolar nucleus is sufficiently large, MAS cannot remove its effect on the line shape of the central transition and causes second-order broadening with characteristic lineshapes as well as a second-order shift. In order to obtain correct chemical shifts

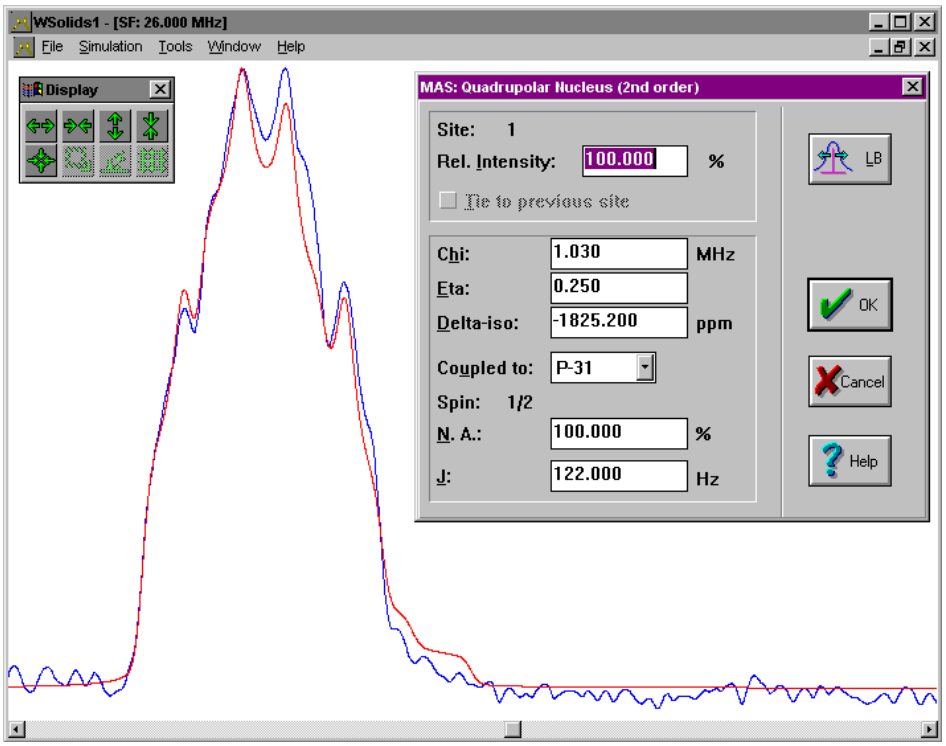


Figure 3.7: Experimental and calculated ^{95}Mo MAS NMR spectra of a powder sample of a molybdenum phosphine complex.

for the quadrupolar nucleus, simulation of the spectra is required. Optionally, indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Implementation Details

Specifically, we use the following convention:

- the NQR notation is used for labelling the axes of the EFG tensor: |VZZ| >= |VYY| >= |VXX|

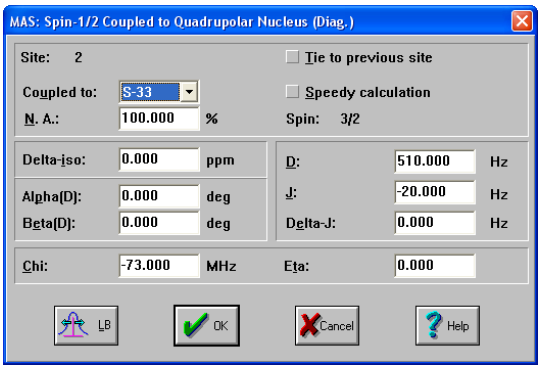
Figure 3.7 shows an example for the succesful simulation of a MAS spectrum of a quadrupolar nucleus that shows the combined effect of quadrupolar interaction and spin-spin coupling to a spin-1/2 nucleus in a powder sample. It is the ^{95}Mo NMR MAS spectrum of pentacarbonyl-5-methyldibenzophosphole molybdenum(0), $Mo(CO)_5$(MeDBP), and the results have been published in:

Solid-State ^{95}Mo NMR Studies of Some Prototypal Molybdenum Compounds: Sodium Molybdate Dihydrate, Hexacarbonylmolybdenum, and Pentacarbonyl Phosphine Molybdenum(0) Complexes.
K. Eichele, R. E. Wasylishen, J. H. Nelson, *J. Phys. Chem. A* **1997**, *101*, 5463-5468, DOI: 10.1021/jp9712415.

References

(1) The second−order expression is taken from Amoureux's treatment, which follows Taulelle: Amoureux, Fernandez, Granger, In *Multinuclear Magnetic Resonance in Liquids and Solids - Chemical Applications*; Granger, Harris, eds.; Kluwer Academic Publishers, 1990; Ch. 22, p 409

3.9 MAS: Spin-1/2 – Spin-S (Diag.)



Spectrum of a powder sample under magic-angle spinning containing a spin-1/2 nucleus dipolar and indirect coupled to a quadrupolar nucleus. The expectation values for the spin states of the quadrupolar nucleus are evaluated using full matrix diagonalization. Only the center peak in the spectrum is calculated (i.e. high-spinning frequency limit).

Note: Don't forget to define the observed nucleus (this is required to evaluate the Larmor frequency of the quadrupolar nucleus).

Note: There can be a problem (p. 48) if the observed nucleus has a negative magnetogyric ratio.

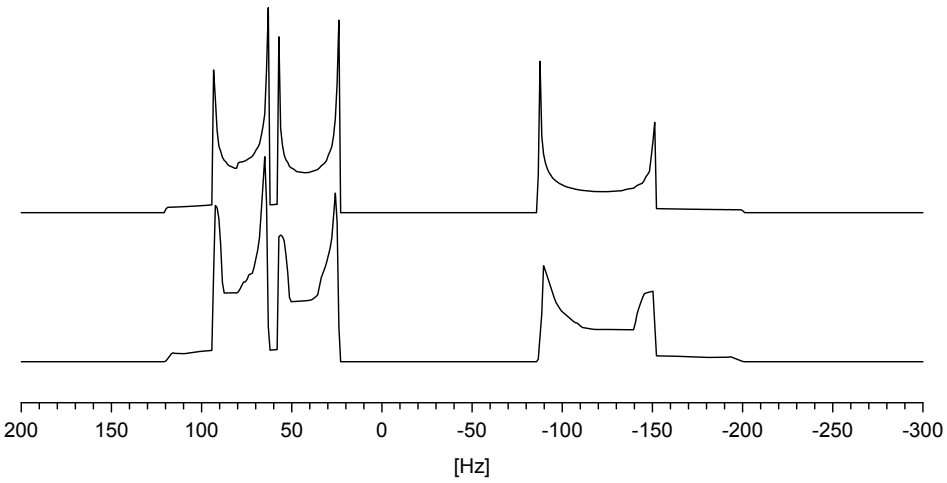
Parameter	Purpose
Coupled to (p. 91)	Specifies the quadrupolar nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
N.A (p. 91)	Natural abundance, in percent, of the coupled nucleus
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Speedy calculation (p. 97)	If checked, less crystallite orientations are included into the calculation; also, the averaging over one rotor period is done in 10° steps rather than 5° steps
Delta-iso (p. 88)	Isotropic chemical shift in ppm
Alpha (p. 92)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
Beta (p. 92)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
D (p. 91)	Direct dipole-dipole coupling constant, in Hz
J (p. 92)	Indirect spin−spin coupling constant, in Hz

Delta-J (p. 92)	Anisotropy of the indirect spin-spin coupling, in Hz
Chi (p. 96)	Quadrupolar coupling constant, in MHz
Eta (p. 96)	Asymmetry parameter of the electric field gradient tensor, 0 <= eta <= 1
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum.

The figure below illustrates the effect a speedy calculation (spectrum at bottom) has on the calculated spectrum:



Implementation Details

Specifically, we use the following conventions:

- the NQR notation is used for labelling the axes of the EFG tensor: |VZZ| >= |VYY| >= |VXX|

Figure 3.8 shows an example for the succesful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to a quadrupolar nucleus in a powder sample. It is the ^{13}C MAS NMR spectrum of a chloroketosulfone, where carbon is coupled to Cl-35 and Cl-37, and the results have been published in:

The Influence of Chlorine-Carbon Dipolar and Indirect Spin-Spin Interactions on High-Resolution Carbon-13 NMR Spectra of Chloroketosulfones in the Solid State.
K. Eichele, R. E. Wasylishen, J. S. Grossert, A. C. Olivieri, *J. Phys. Chem.* **1995**, *99*, 10110-10113, DOI: 10.1021/j100025a010.

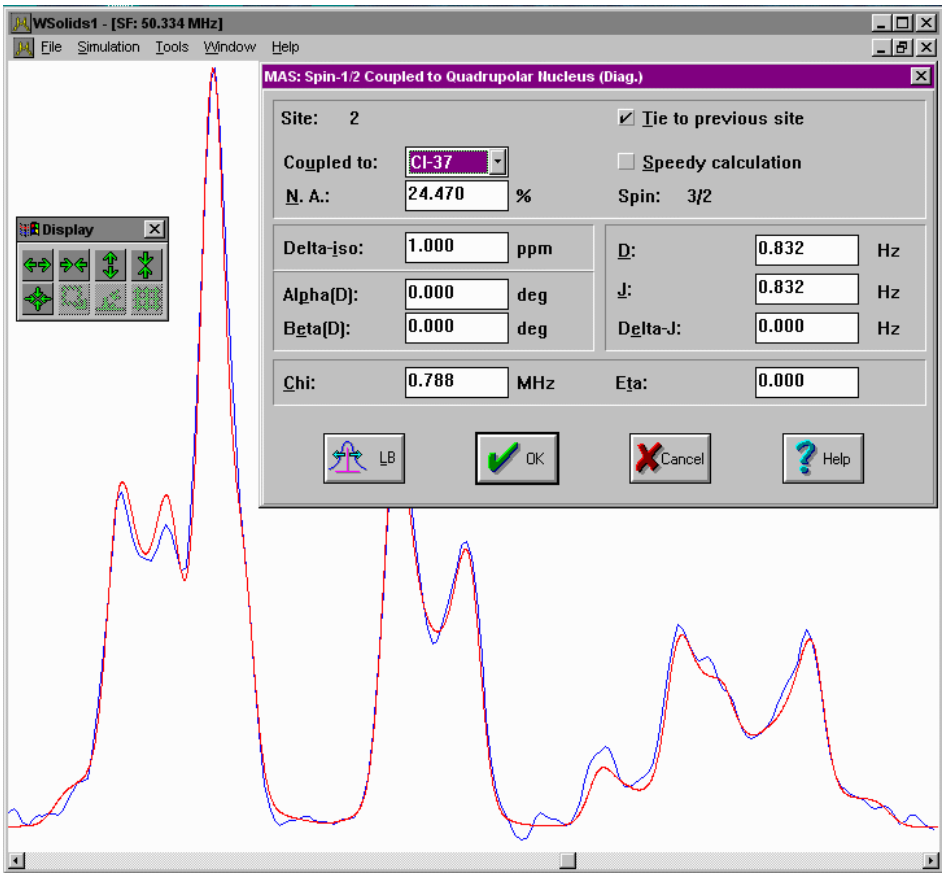
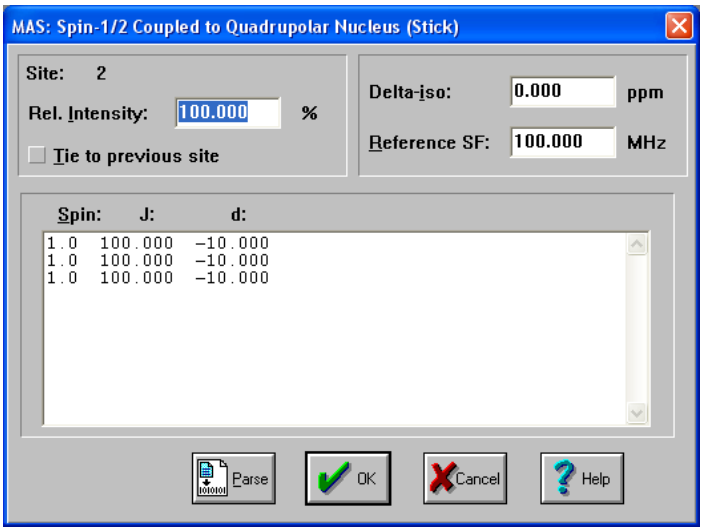


Figure 3.8: Experimental and calculated ^{13}C MAS NMR spectra of a carbon coupled to $^{35/37}$Cl.

This picture also illustrates the workings of the Tie to previous site feature: the parameters of the C-13,Cl-37 isotopologue are tied to those of the C-13,Cl-35 isotopologue by using the ratios of the magnetogyric ratios and nuclear quadrupole moments as factors.

3.10 MAS: Spin-1/2 – Spin-S (Stick)



Calculates the centerband (i.e. high-spinning frequency limit) in the MAS spectrum of a powder sample containing a spin-1/2 nucleus spin-spin coupled to several heteronuclei, typically quadrupolar nuclei. (Actually, one could also calculate solution H-1 NMR spectra of >10 protons coupled to each other, when the spectra are purely first order.) The break-down of the high-field approximation is taken into account using first-order perturbation theory, where the quadrupolar interaction is the perturbation. Each coupling interaction can be described by an indirect spin-spin coupling constant, J, and a field-dependent residual dipolar coupling, d, as well as the number of nuclei coupled and their respective spins.

The program calculates the frequency of each transition and puts some intensity (a "stick") into the corresponding bin of the spectrum array. One may want to use a higher resolution for the calculated spectrum than for the experimental spectrum (e.g. increase the number of points and decrease the spectral width), as the center position of each peak is "quantized" according to the digital resolution.

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site. Except for relative intensity and the spins of the coupled nuclei, all other parameters are affected by the setting of this flag. Always have the site with the most coupled nuclei as first site, followed by decreasing numbers. Otherwise, the result will be unpredictable
Delta-iso (p. 88)	Isotropic chemical shift in ppm
Reference SF	The residual dipolar coupling is field dependent. The value entered for *d* in the edit box is for the spectrometer frequency entered as reference frequency (of the observed nucleus), in MHz. Spectra at different fields can be calculated from the same set of parameters based on different observe frequencies.

Coupled nuclei	In the edit box, enter parameters for each coupled nucleus on a separate line. The parameters **spin**, **J**, and **d** should be separated by blank spaces. To check for proper format, use the Parse button to see the result of how WSolids1interprets the input
Spin	Nuclear spin of the coupled nucleus. This parameter is not affected by the state of the "Tie to previous site" flag
J	Indirect spin-spin coupling constant, in Hz
d	Residual dipolar coupling, in Hz
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box
Parse	Use this button to check if the parameters for the coupled nuclei have been entered correctly

Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum. However, if the quadrupolar and dipolar coupling are small relative to the indirect spin-spin coupling, this so-called breakdown of the high-field approximation causes no significant broadening of the individual peaks, only unequal spacings between the peaks of the multiplet. Such spectra can be simulated using first-order perturbation theory with a stick approach, where the patterns are characterized by an indirect spin-spin coupling constant, J, and a residual dipolar coupling, d.

Implementation Details

If the contribution of the residual dipolar coupling to the actual line shape is small, the resonance frequencies in the MAS NMR spectrum of a spin-1/2 nucleus coupled to a quadrupolar spin-S nucleus are given by [3]:

$$\nu_m = \nu_{\text{iso}} - m|J| - \frac{S(S+1) - 3m^2}{S(2S-1)}\, d \tag{3.1}$$

where ν_{iso} is the frequency of the uncoupled I nucleus, m is the z-component of the angular momentum of the $|m>$ state of nucleus S, *i.e.*, m = S, S - 1, ..., -S. The residual dipolar coupling, d, is given by:

$$d = -\frac{3\chi D}{20Z}\left(3\cos^2\beta^D - 1 + \eta\,\sin^2\beta^D\,\cos 2\alpha^D\right) \tag{3.2}$$

with the quadrupolar coupling constant, $\chi = e^2Qq_{zz}/h$, the asymmetry parameter of the EFG tensor, η = (q_{xx} - q_{yy})/q_{zz}, with principal values $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$, and the Larmor frequency, $Z = \gamma_S$

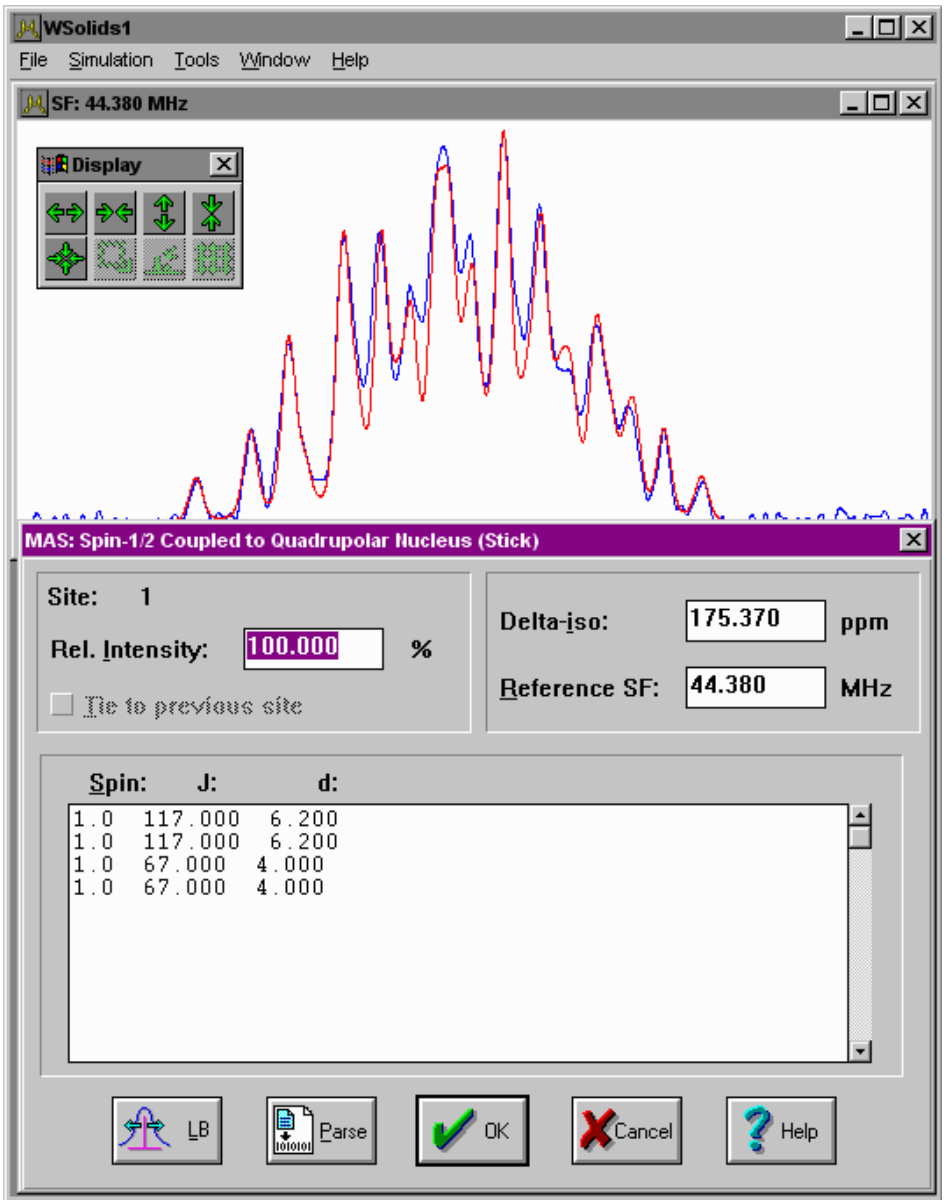


Figure 3.9: Experimental and calculated ^{113}Cd MAS NMR spectra showing coupling to ^{14}N.

$B_0/2\pi$, of the S nucleus. The dipolar coupling constant D is given by

$$D = \left(\frac{\mu_0}{4\pi}\right)\frac{\gamma_I\,\gamma_S}{r_{IS}^3}\left(\frac{\hbar}{2\pi}\right) \tag{3.3}$$

and the azimuthal and polar angles, α^D and β^D, define the orientation of the dipolar vector, r_{IS}, with respect to the principal axis system of the EFG tensor. In systems where anisotropy in **J** has to be considered, the parameter D in Eq. [3.2] is replaced by an effective dipolar coupling constant D' = D - $\Delta J/3$, with $\Delta J = J_{||}$ - $J_{\perp}$, and $J = (J_{||} + 2J_{\perp})/3$, assuming axial symmetry for **J** and $J_{||}$ parallel to r_{IS}.

Figure 3.9 shows an example for the succesful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to several quadrupolar nuclei in a powder sample. It is the ^{113}Cd MAS NMR spectrum of $(NMe_4)_2[Cd(SCN)_4]$, where the octahedral cadmium is coupled to four N-14 nuclei. The results and several other examples have been published in Ref. [5].

References

1. Olivieri, A. C.; Frydman, L.; Diaz, L. E. *J. Magn. Reson.* **1987**, *75*, 50-62.
2. Olivieri, A.; Frydman, L.; Grasselli, M.; Diaz, L. *Magn. Reson. Chem.* **1988**, *26*, 615-618.
3. Olivieri, A. C. *J. Magn. Reson.* **1989**, *81*, 201-205, DOI: 10.1016/0022-2364(89)90281-3.
4. Harris, R. K.; Olivieri, A. C. *Progr. NMR Spectrosc.* **1992**, *24*, 435-456, DOI: 10.1016/0079-6565(92)80004-Y.
5. K. Eichele, R. E. Wasylishen, *Inorg. Chem.* **1994**, *33*, 2766-2773, DOI: 10.1021/ic00091a017.

3.11 MAS: Spin-1/2 – Spin-S (Shape)

Spectrum of a powder sample under magic-angle spinning containing a spin-1/2 nucleus spin-spin coupled to a quadrupolar nucleus. The expectation values for the spin states of the quadrupolar nucleus are evaluated using first-order perturbation theory, where the quadrupolar interaction is the perturbation. Only the center peak in the spectrum is calculated (i.e. high-spinning limit).

Note: Don't forget to define the observed nucleus (this is required to evaluate the Larmor frequency of the quadrupolar nucleus).

Note: For a nucleus with a nuclear spin of 3, a warning will appear that the spectrum contains a single line subspectrum. According to the line shape equation, this will generally be true of two transitions and independent of the parameters used.

Parameter	Purpose
Coupled to (p. 91)	Specifies the quadrupolar nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
N.A (p. 91)	Natural abundance, in percent, of the coupled nucleus
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Delta-iso (p. 88)	Isotropic chemical shift in ppm
Alpha (p. 92)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
Beta (p. 92)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
D (p. 91)	Direct dipole-dipole coupling constant, in Hz
J (p. 92)	Indirect spin−spin coupling constant, in Hz
Delta-J (p. 92)	Anisotropy of the indirect spin-spin coupling, in Hz
Chi (p. 96)	Quadrupolar coupling constant, in MHz
Eta (p. 96)	Asymmetry parameter of the electric field gradient tensor, 0 <= eta <= 1
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

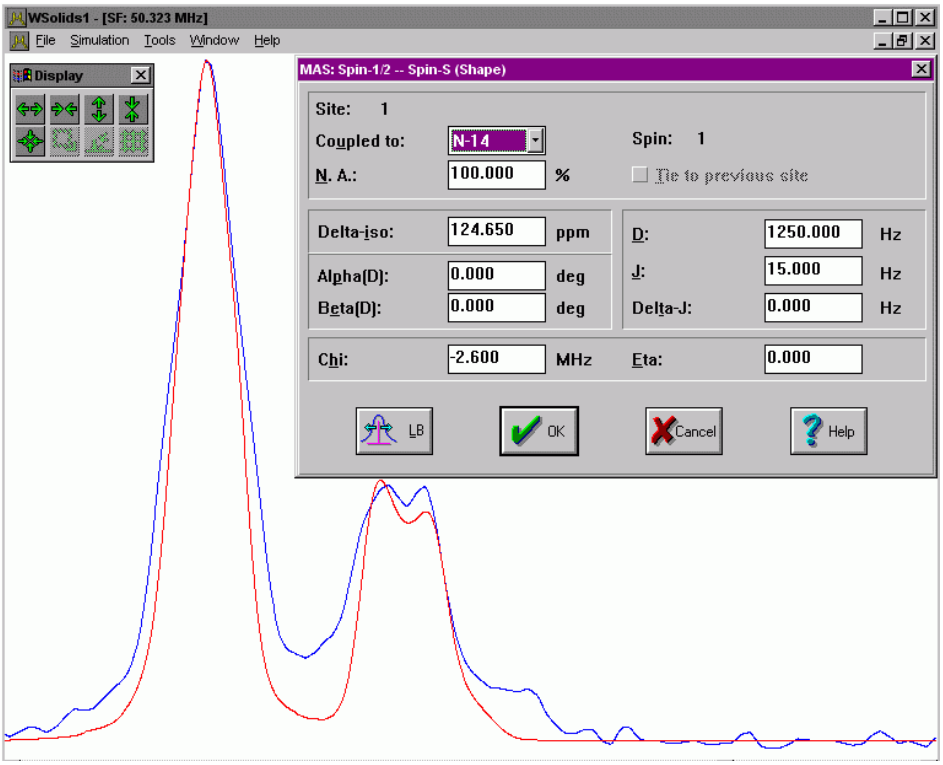


Figure 3.10: Experimental and calculated ^{13}C MAS NMR spectra showing coupling to ^{14}N.

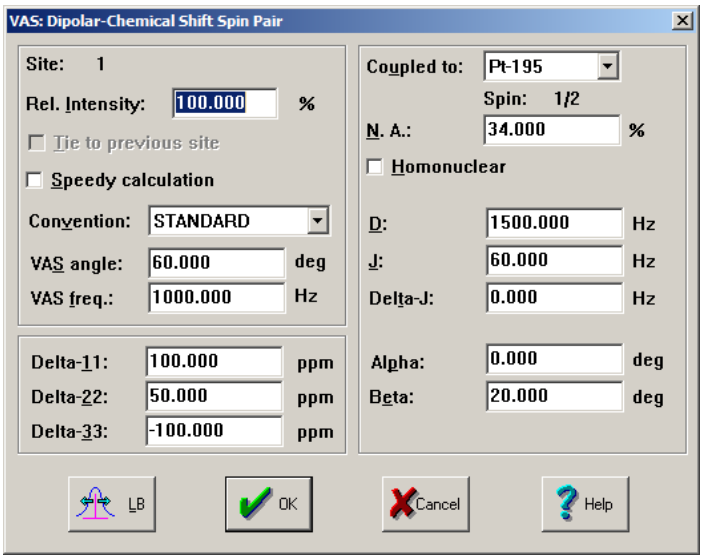
Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum. However, if the quadrupolar coupling is relatively small, this so-called breakdown of the high-field approximation causes lineshapes that can be simulated using first-order perturbation theory. If the broadening is small, such lineshapes can also be analyzed using a "stick" approach.

Figure 3.10 shows an example for the succesful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to several quadrupolar nuclei in a powder sample. It is the ^{13}C MAS NMR spectrum of $(NH_4)SeCN$, where carbon is coupled to a N-14 nucleus, and the results have been published in:

Nuclear Magnetic Shielding Tensors for the Carbon, Nitrogen and Selenium Nuclei of Selenocyanates - A Combined Experimental and Theoretical Approach.
G. M. Bernard, K. Eichele, G. Wu, C. Kirby, R. E. Wasylishen, *Can. J. Chem.* **2000**, *78*, 614-625, DOI: 10.1139/v00-046.

3.12 VAS: Dipolar-Chemical Shift (A2, AX)



Spectrum of a powder sample under variable-angle spinning containing a spin pair where AX or A_2 approximation is valid. Most parameters are described in the section on the static case: Static: Dipolar Chemical Shift (A2, AX) (p. 52). In addition, the following parameters need to be specified:

Parameter	Purpose
VAS angle (p. 97)	The angle of the spinning axis with respect to the external magnetic field, B_0
VAS rate (p. 97)	The spinning frequency, in Hz. Specify a rate greater than the spectrum width to calculate the high spinning speed limit.

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. Spinning the powder sample rapidly about an axis that forms an angle different from the magic angle with respect to the external magnetic field, the resulting lineshape will look like that of a static powder sample, but scaled by a factor that depends on the spinning angle. This scaling factor ranges from 1.0 (for spinning parallel to the field) to -0.5 (for spinning perpendicular to the magnetic field).

In versions of WSolids1 before 1.21, this model would calculate the line shape of the isotropic peak in the so-called high-spinning speed limit, where no spinning sidebands play a role. Experimentally, this can be achieved by adding the line shapes of the spinning sidebands to that of the isotropic peak (or by rotor synchronized sampling). Note that this high-spinning speed limit is sometimes called the infinite spinning speed limit incorrectly. Here, we are still assuming that the Zeeman interaction is the greatest interaction and hence the Larmor frequency greater than the spinning speed. Infinite spinning would require modification of the theory!

In versions of WSolids1 1.21 and onward, the calculation of spinning sidebands was included. If you still want to use the high spinning speed limit, enter a spinning frequency that is wider than the spectrum width. If your spectrum default parameters are such that part of the line shape of a

spinning sideband is outside the spectrum window, you may receive a warning message about contributions outside the spectrum window. Consider increasing the width of the spectrum. Also, the relative intensities of the sites might be represented erroneously if significant spinning sidebands are outside the calculated spectrum width, because the scaling is based on the integral of the spectrum.

Figure 3.11 shows an example for the succesful simulation of a spectrum arising from the combined effect of chemical shift anisotropy, and heteronuclear indirect and dipolar coupling in a powder sample under fast variable-angle spinning. It is the 31P NMR spectrum of a cadmium phosphine complex.

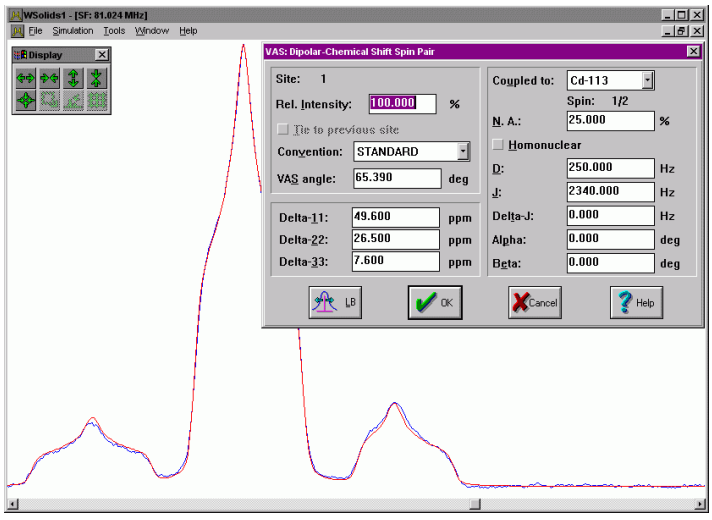
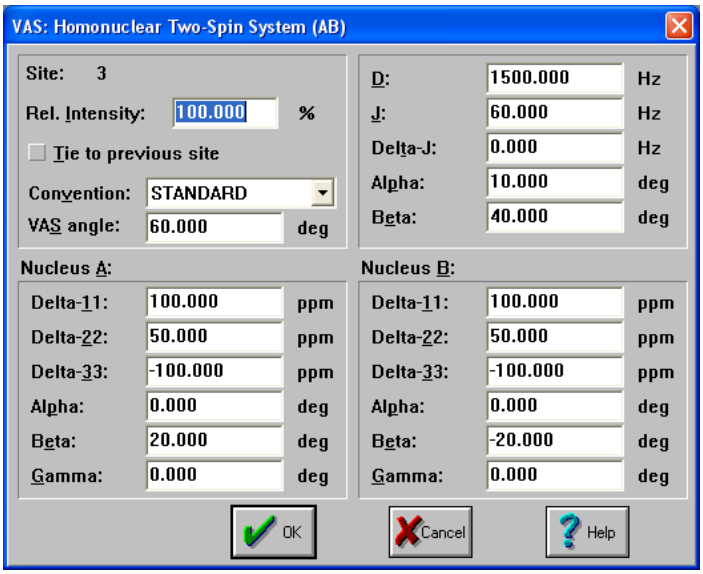


Figure 3.11: Experimental and calculated ^{31}P VAS NMR spectra of a cadmium phosphine complex.

3.13 VAS: Dipolar-Chemical Shift (AB)



Spectrum of a powder sample under variable-angle spinning containing a homonuclear spin pair, using AB equation.

Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. Spinning the powder sample rapidly about an axis that forms an angle different from the magic angle with respect to the external magnetic field, the resulting lineshape will look like that of a static powder sample, but scaled by a factor that depends on the spinning angle. This scaling factor ranges from 1.0 (for spinning parallel to the field) to -0.5 (for spinning perpendicular to the magnetic field).

Figure 3.12 shows an example for the succesful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear indirect and dipolar coupling in a powder sample under fast variable-angle spinning. It is the ^{31}P NMR spectrum of *fac*-(OC)$_3$(η^2-phen)Mo(η^1-Ph_2P-PPh_2), and the results have been published in:

Phosphorus-31 Solid-State NMR Studies of Homonuclear Spin Pairs in Molybdenum Phosphine Complexes: Single-Crystal, Dipolar-Chemical Shift, Rotational-Resonance and 2D Spin-Echo NMR Experiments.
K. Eichele, G. Ossenkamp, R. E. Wasylishen, T. S. Cameron, J. F. Britten, *Inorg. Chem.* **1999**, *38*, 639-651, DOI: 10.1021/ic9806232.

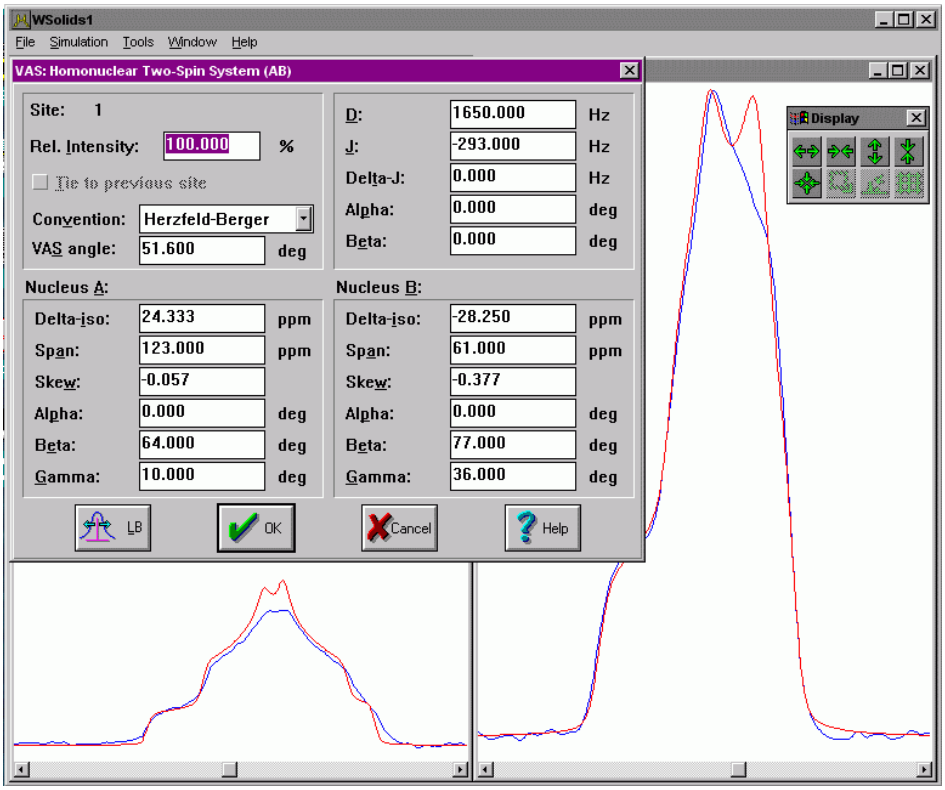
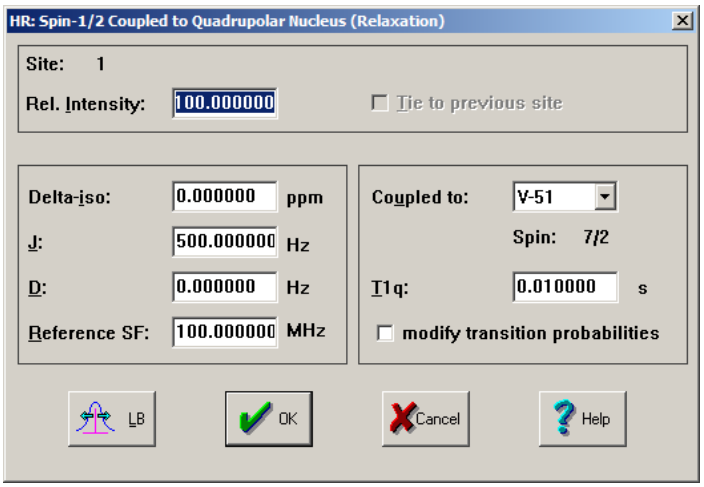
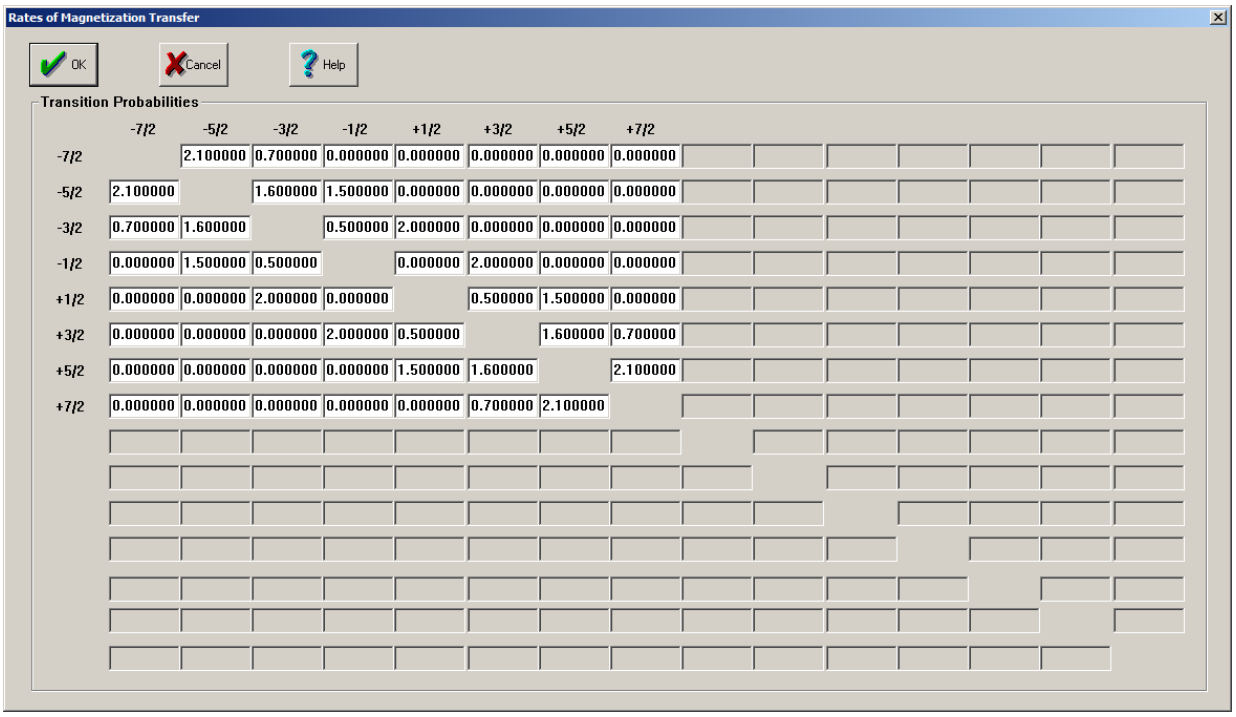


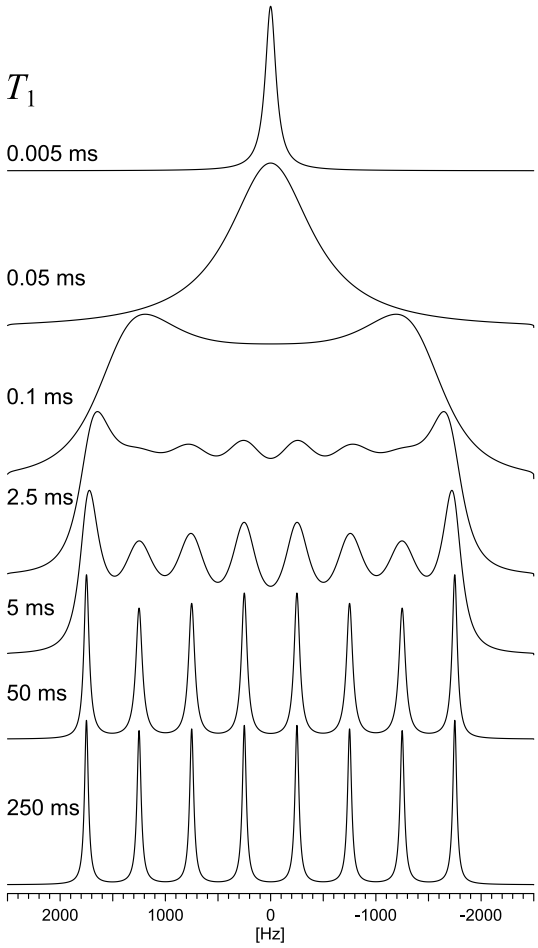
Figure 3.12: Experimental and calculated ^{31}P VAS NMR spectra of a molybdenum phosphine complex.

3.14 HR: Spin-1/2 Coupled to Quadrupolar Nucleus (Relaxation)





This model is actually intended for the calculation of the solution spectrum (HR = high-resolution $\approx$ solution) of a spin-1/2 nucleus (spin I in the following) coupled to a quadrupolar nucleus S where the spin-lattice relaxation of the quadrupolar nucleus affects the spectrum of the spin-1/2 nucleus. A few modifications were introduced to accomodate the simulation of solid state spectra in limited cases where first order perturbation theory is valid (model MAS: Spin-1/2 – Spin-S (Stick) (p. 70)). If necessary, the individual elements of the transfer probabilities matrix (see below) can be modified. Some example spectra are illustrated below for the following spin system: ^{31}P coupled to ^{51}V (I = 7/2), with $J(^{51}\text{V},^{31}\text{P})$ = 500 Hz, an LB of 40 Hz, and the ^{51}V spin-lattice relaxation times T_1 indicated in the figure. At intermediate T_1's, the apparent unequal intensities within the non-binomial octet are the result of the different life times of the associated ^{51}V spin states, causing different line widths and hence different peak heights (but equal integrals).



Note: For each point in the spectrum, the chemical shift matrix is constructed and added to the relaxation matrix, the result is inverted and the probabilities evaluated. This is a time consuming process, therefore limit the spectrum limits to the region of interest and only use as many spectrum points (SI) as necessary.

Parameter	Purpose
Rel. Intensity (p. 88)	Relative intensity of this site in percent
Tie to previous site (p. 88)	Ties parameters to those of the previous site
Coupled to (p. 91)	Specifies the quadrupolar nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
Delta-iso (p. 88)	Isotropic chemical shift in ppm
J (p. 92)	Indirect spin−spin coupling constant, in Hz
d	Residual dipolar coupling, in Hz (see model MAS: Spin-1/2 – Spin-S (Stick) (p. 70))

Reference SF	The residual dipolar coupling is field dependent. The value entered for d in the edit box is for the spectrometer frequency entered as reference frequency (of the observed nucleus), in MHz. Spectra at different fields can be calculated from the same set of parameters based on different observe frequencies.
T1q	The spin-lattice relaxation time, in seconds, of the coupled nucleus due to the quadrupolar interaction at the coupled nucleus
modify transition probabilities	Provides access to the individual matrix elements R_{jk} representing the transition probabilities (see below). On first call, the matrix is initialized according to the expressions given below
LB (p. 32)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the Spectrum Default Parameters (p. 28) box

Background

Implementation Details

The implementation of this spin system is based on the approach summarized by Abragam [1], but instead of working with one "complex" complex matrix, (**A** in Abragam [1]), the different parameters are separated into different matrices, following Whitesides [2]:

$$I(\omega) \quad \propto \quad \mathrm{Re}\left[\mathbf{W}\,(\mathbf{A})^{-1}\cdot\mathbf{1}\right] \tag{3.4}$$

$$\mathbf{A} \quad = \quad \mathbf{\Omega} + \frac{1}{T_{1Q}}\mathbf{R} + \mathbf{K} \tag{3.5}$$

where:

W: a row vector with components proportional to the a priori probabilities of the $(2S+1)$ spin states of the nucleus; in most papers, all are equal to 1: $\mathbf{W} = \{\mathbf{1}.....\mathbf{1}\}$;

however, here we set the elements to $(2S+1)^{-1}$, following Kempgens [3].

1: a $(2S+1)$ unit column vector

Ω: a $(2S+1)\times(2S+1)$ diagonal complex matrix with elements corresponding to shifts and couplings, ordered in terms of increasing m_S:

$$\Omega_{m,m'} = i(\omega_0 - \omega + m2\pi J - 2\pi\frac{S(S+1)-3m^2}{S(2S-1)}\,d)\,\delta_{m,m'}$$

K: a diagonal matrix whose elements determine the line widths of spin I in absence of contributions from relaxation of spin S,

$$K_{mm} = -1/T_2$$

Abragam [1] and other authors neglect this contribution, the only author that uses this separate matrix is Whitesides [2]. In WSolids1, this matrix is currently not used because it would only allow for Lorentzian line shapes. Instead, the line shape is convoluted after the actual calculation.

R: a matrix describing the rates of transfer of magnetization between sites corresponding to different values of m_S. Usually, the matrix also includes T_{1q}, but here we put it in front of the matrix in order to be able to deal with the transition probabilities R_{jk} more easily, in case they deviate from the value derived from the expressions below. The diagonal elements of **R**, $R_{m,m}$, are the appropriate row sums:

$$\frac{1}{T_{1q}} = \frac{3\pi^2}{10}\frac{(2S+3)}{S^2(2S-1)}\chi^2[1+\frac{1}{3}\eta^2]\tau$$

$$R_{m,m\pm1} = \frac{(2m\pm1)^2(S\pm m+1)(S\mp m)}{2(2S-1)(2S+3)} \tag{3.6}$$

$$R_{m,m\pm2} = \frac{(S\mp m)(S\mp m-1)(S\pm m+1)(S\pm m+2)}{2(2S-1)(2S+3)} \tag{3.7}$$

$$R_{m,m} = -\sum_{m\prime}^{m\prime\neq m} R_{m,m\prime} \tag{3.8}$$

where, according to $\frac{1}{T_{1q}}R_{m,m} = -1/\tau_m$, this element is related to the average life time τ_m of state m.
E.g., for different spins, this matrix is:

$S=1$	-1	0	+1
-1	$\frac{-6}{10}$	$\frac{2}{10}$	$\frac{4}{10}$
0	$\frac{2}{10}$	$\frac{-4}{10}$	$\frac{2}{10}$
+1	$\frac{4}{10}$	$\frac{2}{10}$	$\frac{-6}{10}$

$S=3/2$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$-\frac{3}{2}$	-1	$\frac{1}{2}$	$\frac{1}{2}$	0
$-\frac{1}{2}$	$\frac{1}{2}$	-1	0	$\frac{1}{2}$
$\frac{1}{2}$	$\frac{1}{2}$	0	-1	$\frac{1}{2}$
$\frac{3}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$	-1

$S=5/2$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
$-\frac{5}{2}$	$-\frac{120}{64}$	$\frac{80}{64}$	$\frac{40}{64}$	0	0	0
$-\frac{3}{2}$	$\frac{80}{64}$	$-\frac{184}{64}$	$\frac{32}{64}$	$\frac{72}{64}$	0	0
$-\frac{1}{2}$	$\frac{40}{64}$	$\frac{32}{64}$	$-\frac{144}{64}$	0	$\frac{72}{64}$	0
$\frac{1}{2}$	0	$\frac{72}{64}$	0	$-\frac{144}{64}$	$\frac{32}{64}$	$\frac{40}{64}$
$\frac{3}{2}$	0	0	$\frac{72}{64}$	$\frac{32}{64}$	$-\frac{184}{64}$	$\frac{80}{64}$
$\frac{5}{2}$	0	0	0	$\frac{40}{64}$	$\frac{80}{64}$	$-\frac{120}{64}$

$S=3$	-3	-2	-1	0	1	2	3
-3	$-\frac{7}{3}$	$\frac{5}{3}$	$\frac{2}{3}$	0	0	0	0
-2	$\frac{5}{3}$	-4	1	$\frac{4}{3}$	0	0	0
-1	$\frac{2}{3}$	1	$-\frac{51}{15}$	$\frac{2}{15}$	$\frac{8}{5}$	0	0
0	0	$\frac{4}{3}$	$\frac{2}{15}$	$-\frac{44}{15}$	$\frac{2}{15}$	$\frac{4}{3}$	0
1	0	0	$\frac{8}{5}$	$\frac{2}{15}$	$-\frac{51}{15}$	1	$\frac{2}{3}$
2	0	0	0	$\frac{4}{3}$	1	-4	$\frac{5}{3}$
3	0	0	0	0	$\frac{2}{3}$	$\frac{5}{3}$	$-\frac{7}{3}$

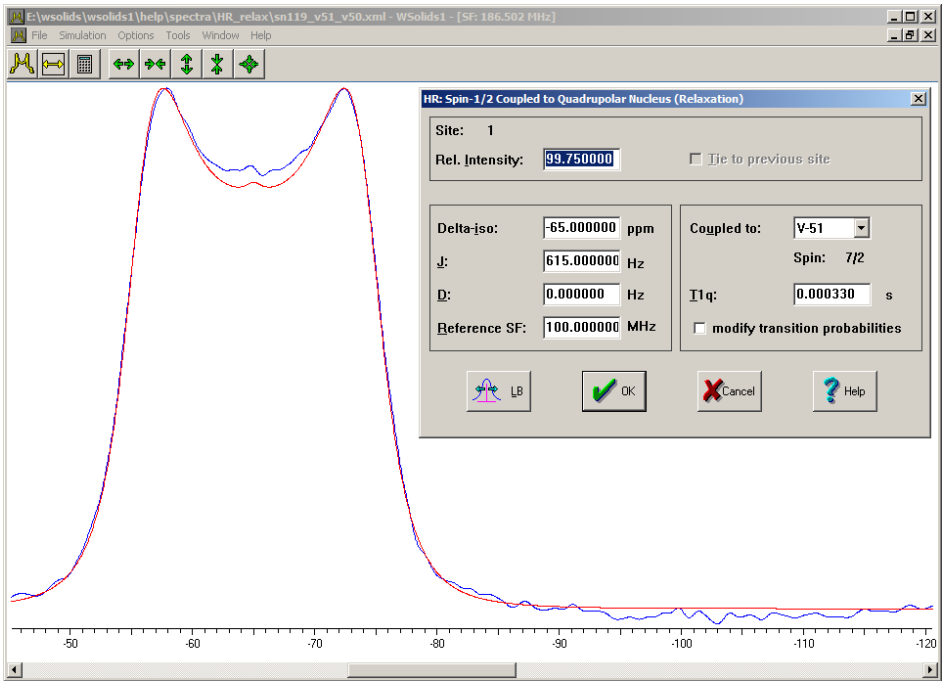


Figure 3.13: Experimental and calculated high-resolution (solution) ^{119}Sn NMR spectra of tin coupled to a ^{51}V nucleus showing the effect of relaxation.

$S = 7/2$	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
$-\frac{7}{2}$	$-\frac{14}{5}$	$\frac{21}{10}$	$\frac{7}{10}$	0	0	0	0	0
$-\frac{5}{2}$	$\frac{21}{10}$	$-\frac{26}{5}$	$\frac{8}{5}$	$\frac{3}{2}$	0	0	0	0
$-\frac{3}{2}$	$\frac{7}{10}$	$\frac{8}{5}$	$-\frac{24}{5}$	$\frac{1}{2}$	2	0	0	0
$-\frac{1}{2}$	0	$\frac{3}{2}$	$\frac{1}{2}$	-4	0	2	0	0
$\frac{1}{2}$	0	0	2	0	-4	$\frac{1}{2}$	$\frac{3}{2}$	0
$\frac{3}{2}$	0	0	0	2	$\frac{1}{2}$	$-\frac{24}{5}$	$\frac{8}{5}$	$\frac{7}{10}$
$\frac{5}{2}$	0	0	0	0	$\frac{3}{2}$	$\frac{8}{5}$	$-\frac{26}{5}$	$\frac{21}{10}$
$\frac{7}{2}$	0	0	0	0	0	$\frac{7}{10}$	$\frac{21}{10}$	$-\frac{14}{5}$

These are the matrix elements that can be modified if the item *modify transition probabilities* is checked in the parameter input dialog box (compare the elements of the matrix shown in the table for $S = 7/2$ above to the second dialog shown for this calculation model (p. 80)). On first call, the elements are initialized using eqs. 3.6 and 3.7 and can be modified by the user, e.g. to accomodate deviations from the extreme narrowing limit or cross terms.

Figure 3.13 shows an example of the simulation of a ^{119}Sn spectrum arising from coupling of tin to vanadium; the small feature in the center was produced by considering, just for fun, not only ^{51}V but also ^{50}V. In order to convert the necessary parameters for one isotope to those of the other isotope for use with the Tie to previous site (p. 88) feature, I have used:

- for the spin-spin coupling constant:

$$J(\text{V-50}) = \frac{\gamma(\text{V-50})}{\gamma(\text{V-51})}\, J(\text{V-51}) = 0.379 \times J(\text{V-51})$$

- for the relaxation rate: the rate of quadrupolar relaxation is given by

$$\frac{1}{T_{1Q}} = \frac{3}{40}\frac{\chi^2\tau(2S+3)}{S^2(2S-1)}$$

where (see electric field gradient (p. 96))

$$\chi = \frac{eV_{ZZ}Q}{h} = \frac{e^2q_{ZZ}Q}{h}$$

In molecules which differ only in having different isotopes of the same element, the electric field gradient at that elements' nuclei, eq_{ZZ}, will be close to identical for the isotopes while the rotational correlation time for molecular motion will scarcely be altered by the substitution (at least for heavy isotopes, where the relative differences between the masses of the isotopologues will be small).

The equation can thus be simplified to

$$\frac{1}{T_{1Q}} \propto Q^2 f(S)$$

where $f(S) = \frac{(2S+3)}{S^2(2S-1)}$; values of S and corresponding values of $f(S)$ are:

S	1	$\frac{3}{2}$	$\frac{5}{2}$	3	$\frac{7}{2}$	$\frac{9}{2}$	6
$f(S)$	5	1.33	0.32	0.2	0.136	0.074	0.0379

Hence, the value of S is extremely important when comparing the relaxation behaviour of nuclei of different S, an increase in S having the opposite effect to an increase in eQ.

Therefore,

$$T_1(\text{V-50}) = \left(\frac{Q(\text{V-51})}{Q(\text{V-50})}\right)^2 \frac{f(S=5/2)}{f(S=6)} \times T_1(\text{V-51}) = 0.220 \times T_1(\text{V-51})$$

(Actually, in Fig. 3.13 I have used a T_1 factor somewhat smaller than calculated above, 0.1 instead of 0.22, to make the ^{50}V feature a little sharper. Here, I just wanted to demonstrate how to deal with isotopologues.)

References

(1) A. Abragam, *The Principles of Nuclear Magnetism*; Clarendon Press, Oxford, 1961

(2) G. M. Whitesides, H. L. Mitchell, *J. Am. Chem. Soc.* **1969**, *91*, 2245-2250. DOI: 10.1021/ja01037a011

(3) P. Kempgens, J. Hirschinger, K. Elbayed, J. Raya, P. Granger, J. Rosé, *J. Phys. Chem.* **1996**, *100*, 2045-2052. DOI: 10.1021/jp9524486

4 Spin System Parameters

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4.1 Relative Intensity

The **relative intensity** of each site determines the relative area this site contributes to the total line shape. Allowed values are 0-100, but there is no check whether the relative intensities of all sites sum up to 100 %. Considered as a mere scaling factor.

To exclude a site momentarily from a calculation without deleting it, set the relative intensity of this site to zero.

4.2 Tie to previous site

This feature allows to tie the parameters of a site to the parameters of the previous site, using fixed factors. Such a feature is useful if the spectrum is made up of a variety of different isotopologues and the site specific parameters differ only by ratios of nuclear constants. Because such cases are rather rare, the implementation here does not offer a high degree of sophistication.

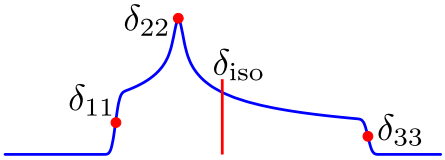
There are a few points to keep in mind:

- More than one site needs to be available, and this feature will not be available for the first site (obviously)
- The simulation models for the sites tied together should be the same. This is not checked! Tying together different models may produce unexpected results
- Once sites are tied together, one cannot change the convention used for tensor components
- Parameters not affected by the state of the **Tie** check box are grouped together with this check box in one shaded area; all parameters outside this area depend on the state of the check box (exceptions are, e.g., spin quantum numbers)

4.3 Convention

Unfortunately, there are many different conventions around in the literature for labeling the principal components of chemical shift tensors. Most of the conventions have advantages for certain situations but drawbacks in others. Often, it is not obvious which convention has been chosen. The collection given here attempts to summarize some of the most frequently used conventions.

4.3.1 Standard Convention



Principal Components	$\delta_{11} \geq \delta_{22} \geq \delta_{33}$
	$\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$
Isotropic Value	$\delta_{\mathrm{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
	$\sigma_{\mathrm{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$

In what we shall call the standard convention [1,3], the principal components of the chemical shift tensor, δ_{11}, δ_{22}, and δ_{33}, are labeled according to the IUPAC rules [2]. They follow the high frequency-positive order. Thus, δ_{11} corresponds to the direction of least shielding, σ_{11}, with the highest frequency, while δ_{33} corresponds to the direction of highest shielding, σ_{33}, with the lowest frequency. The isotropic values, δ_{iso} or σ_{iso}, are the average values of the principal components, and correspond to the center of gravity of the line shape.

In many cases, the spectrum or calculation will not depend on any given order, and the values can be entered in any order. However, in some cases where the orientation of the tensors is also important, the assignment of values to the principal axes will affect the spectrum.

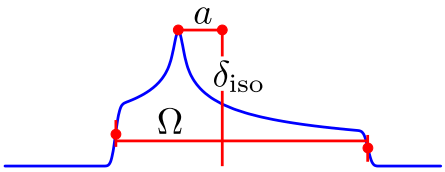
References

1 J. Mason, *Solid State Nucl. Magn. Reson.* **1993**, *2*, 285, DOI: 10.1016/0926-2040(93)90010-K.

2 R. N. Jones, A. R. H. Cole, F. A. Miller, M. A. Elyashévich, T. Förster, A. Hadni, Y. Morino, N. Sheppard, E. Fluck, E. R. Lippincott, R. C. Lord, S. Nagakura, J. Plivá, Sir H. Thompson, D. W. Turner, G. Herzberg, T. Urbanski, *Pure Appl. Chem.* **1972**, *29*, 625-628, DOI: 10.1351/pac197229040625.

3 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure Appl. Chem.* **2008**, *80*, 59-84, DOI: 10.1351/pac200880010059.

4.3.2 Herzfeld-Berger Convention



Isotropic Value	$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
Span	$\Omega = \delta_{11} - \delta_{33} \quad (\Omega \geq 0)$
Skew	$\kappa = 3(\delta_{22} - \delta_{iso})/\Omega; (-1 \leq \kappa \leq 1)$

In the Herzfeld-Berger notation [1], a tensor is described by three parameters, which are combinations of the principal components in the standard notation:
The **isotropic value**, i.e., the center of gravity, is the average value of the principal components.
The **span** describes the maximum width of the powder pattern.
The **skew** of the tensor is a measure of the amount and orientation of the asymmetry of the tensor. As indicated, κ is given by $3a$ / Ω, where $a = (\delta_{22} - \delta_{iso})$. Depending on the position of δ_{22} with respect to δ_{iso}, the sign is either positive or negative. If δ_{22} equals δ_{iso}, a and the skew are zero. In the case of an axially symmetric tensor, δ_{22} equals either δ_{11} or δ_{33} and $a = \pm\Omega/3$. Hence, the skew is ± 1.

The parameter μ used with the Herzfeld-Berger tables is related to the span of a tensor by:
$\mu = \Omega$ * SF / spinning rate

The parameter ρ used with the Herzfeld-Berger tables corresponds to the skew of a tensor described here. For "historical" reasons we used ρ throughout this manual, but generally we prefer κ [2].

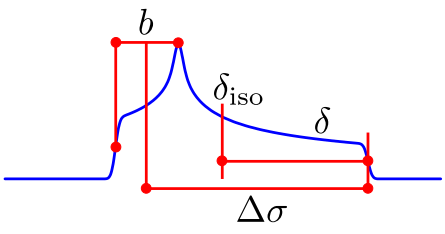
The Herzfeld-Berger convention is related to the Standard convention via:
$\delta_{22} = \delta_{iso} + (\kappa\ \Omega\ /\ 3)$
$\delta_{33} = (\ 3\ \delta_{iso} - \delta_{22} - \Omega\ )\ /\ 2$
$\delta_{11} = 3\ \delta_{iso} - \delta_{22} - \delta_{33}$

References

1 J. Herzfeld, A. E. Berger, *J. Chem. Phys.* **1980**, *73*, 6021-6030, DOI: 10.1063/1.440136.

2 J. Mason, *Solid State Nucl. Magn. Reson.* **1993**, *2*, 285, DOI: 10.1016/0926-2040(93)90010-K.

4.3.3 Haeberlen Convention



Principal Components	$\lvert\delta_{zz} - \delta_{iso}\rvert \geq \lvert\delta_{xx} - \delta_{iso}\rvert \geq \lvert\delta_{yy} - \delta_{iso}\rvert$
Isotropic Value	$\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
Reduced Anisotropy	$\delta = \delta_{zz} - \delta_{iso}$
Anisotropy	$\Delta\sigma = \delta_{zz} - (\delta_{xx} + \delta_{yy})/2 = 3\delta/2$
Asymmetry	$\eta = (\delta_{yy} - \delta_{xx})/\delta; (0 \leq \eta \leq +1)$

The Haeberlen-Mehring [1,2] convention uses different combinations of the principal components to describe the line shape. This convention requires that the principal components are ordered according to their separation from the isotropic value.

The center of gravity of the line shape is described by the **isotropic value**, which is the average value of the principal components.

The **anisotropy** and **reduced anisotropy** describe the largest separation from the center of gravity. (The term reduced anisotropy is not used in the literature, but we introduce it here in order to be able to distinguish between δ and $\Delta\sigma$.) The sign of the anisotropy indicates on which side of the isotropic value one can find the largest separation.

The **asymmetry** parameter indicates by how much the line shape deviates from that of an axially symmetric tensor. In the case of an axially symmetric tensor, $b = (\delta_{yy} - \delta_{xx})$ will be zero and hence $\eta = 0$.

The Haeberlen-Mehring convention is related to the Standard convention via:

for $\delta > 0$ (i.e. $\delta_{zz} = \delta_{11}$)	for $\delta < 0$ (i.e. $\delta_{zz} = \delta_{33}$)
$\delta_{11} = \delta_{iso} + \delta$	$\delta_{33} = \delta_{iso} + \delta$
$\delta_{22} = \delta_{iso} - \delta(1-\eta)/2$	$\delta_{22} = \delta_{iso} - \delta(1-\eta)/2$
$\delta_{33} = \delta_{iso} - \delta(1+\eta)/2$	$\delta_{11} = \delta_{iso} - \delta(1+\eta)/2$

References

1 U. Haeberlen, In *Advances in Magnetic esonance*; Suppl. 1; J. S. Waugh, Ed.; Academic Press: New York, 1976.

2 M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd. ed.; Springer Verlag: Berlin, 1983.

4.3.4 Chemical Shift and Magnetic Shielding

It is recommended that the IUPAC conventions [1] are obeyed:

- The **nuclear magnetic shielding**(absolute shielding), σ, in ppm is the difference in shielding between the frequency of the bare nucleus, ν_{nucl}, and the frequency of the same nucleus in the species under investigation, ν_s:
  σ / ppm = 1e06 * (ν_{nucl} - ν_s) / ν_{nucl}
- The **chemical shift**, δ, is the difference in shielding between the nucleus in the species under investigation, σ_s, and the shielding of the same nucleus in a reference compound, σ_{ref}:
  δ / ppm = (σ_{ref} - σ_s) / (1 - σ_{ref})
  Because σ_{ref} is often a small number compared to 1, frequently the following approximation is used:

Shifts, commonly used in solution and solid state NMR studies, are thus positive to high frequency. Absolute shieldings are positive to low frequency, and are only accessible via theoretical calculations. The establishment of a correspondence between a chemical shift scale and a chemical shielding scale is not a trivial task and requires both careful theoretical calculations and experimental measurements [2].

The nuclear magnetic shielding (absolute shielding) is **the** molecular electronic property. The chemical shift is a quantity that we experimentalists have defined and use because of our inability to directly measure the absolute magnetic shielding. This inability results from our inability to know

the magnitude of the magnetic field to an accuracy on the order of parts per billion, independent of the resonance experiment [3].

Comments

The symbol σ should only be used for absolute shieldings. Often, however, authors use a "pseudo" shielding scale, where the "shielding" is obtained by simply reversing the sign of the chemical shift. In our opinion, this adds only to the confusion without providing any additional insight.

Note that the exact formulation of the span (p. 88), Ω, contains the factor (1 - σ_{ref}) [3]:
$\Omega = (\delta_{11} - \delta_{33})\ (1 - \sigma_{ref})$

References

1 *Pure Appl. Chem.* **1972**, *29*, 627; **1976**, *45*, 217.

2 Some examples for established shielding scales:

Carbon:

- A. K. Jameson, C. J. Jameson, *Chem. Phys. Lett.* **1987**, *134*, 461.
- W. T. Raynes, R. McVay, S. J. Wright, *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 759.

Silicon:

- C. J. Jameson, A. K. Jameson, *Chem. Phys. Lett.* **1988**, *149*, 300.

Phosphorus:

- C. J. Jameson, A. De Dios, A. K. Jameson, *Chem. Phys. Lett*. **1990**, *167*, 575.

Tin:

- A. Laaksonen, R. E. Wasylishen, *J. Am. Chem. Soc.* **1995**, *117*, 392.

3 C. J. Jameson, *Solid State Nucl. Magn. Reson.* **1998**, *11*, 265.

4.4 Coupled To

In some models, the observed nucleus is coupled to another nucleus via indirect spin-spin or direct dipole-dipole coupling. The coupled nucleus can be selected from a list of available isotopes. In some cases, this also updates an entry with the natural abundance (p. 91) of the selected isotope as well as the spin of this nucleus.

4.5 Natural Abundance

By default, this parameter is set to the natural abundance of an isotope, in percent. This parameter can, however, be changed to reflect isotopic enrichment.

4.6 Dipolar Coupling Constant D

The direct dipole-dipole coupling is the through-space interaction between the magnetic moments of nuclei. The magnitude of this interaction is characterized by the **Dipolar Coupling Constant**, given in Hz. It depends on the inverse cube of the distance between the interacting nuclei, besides some natural and nuclear constants:

$$D = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{2\pi} \langle r_{IS}^{-3} \rangle$$

In contrast, the indirect spin-spin coupling (p. 92) between nuclear magnetic moments is mediated by intervening electrons.

4.7 Indirect Spin-Spin Coupling J

The **indirect spin-spin coupling** between the magnetic moments of nuclei is mediated by intervening electrons. In contrast to the direct dipole-dipole coupling (p. 91), there is no simple relationship between its magnitude and geometry. In solution NMR studies, the magnitude of this interaction is simply called the spin-spin coupling constant, **J**, reported in Hz. In solid-state NMR, it is more adequately referred to as **isotropic spin-spin coupling constant**, as it is, in principle, anisotropic (p. 92) in nature.

4.8 Anisotropy in Indirect Spin-Spin Coupling Delta-J

The **indirect spin-spin coupling** between the magnetic moments of nuclei is mediated by intervening electrons. This interaction is, in principle, anisotropic in nature. Assuming axial symmetry, the anisotropy of the indirect spin-spin coupling is defined as the difference between the unique component and the perpendicular components:

$$\Delta J = J_{||} - J_{\perp}$$

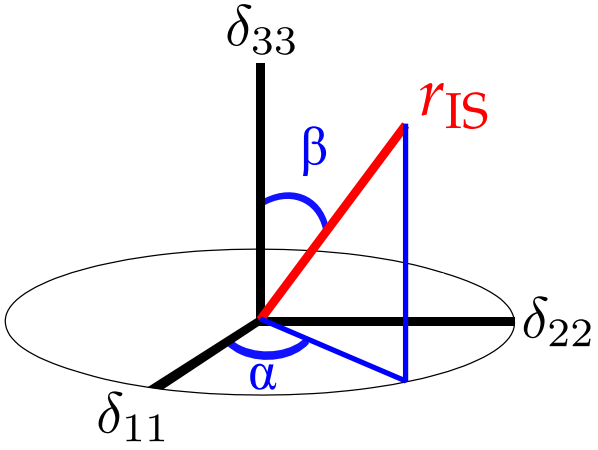
In solution NMR spectra, the anisotropy of the indirect spin-spin coupling does not lead to splittings, although it could provide a mechanism for relaxation. Physically, the anisotropy of the indirect spin spin coupling behaves exactly the same way as the direct dipole-dipole coupling. Therefore, one cannot determine both interactions separately in an experiment, only an effective dipolar coupling constant:

$$D_{eff} = \kappa \left[D - \frac{\Delta J}{3} \right]$$

However, one could calculate the dipolar coupling constant (p. 91) from known internuclear separations (cf. Calculate Dipolar Coupling Constant (p. 41)). For an AX spin system, the prefactor κ of the equation above equals one, $\kappa = 1$, while for a pair of magnetically equivalent spins this factor corresponds to $3/2$, $\kappa = 1.5$

> **Note:** For an A2 spin system, the isotropic part of the indirect spin-spin coupling (p. 92) does not contribute to the spectrum, but the anisotropy of the indirect spin-spin coupling **does!**

4.9 Polar Angles

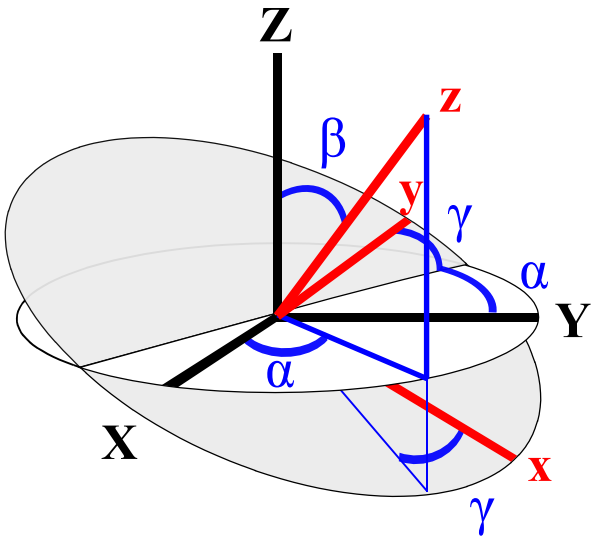


Polar angles are used to define the orientation of a vector in a three-dimensional Cartesian coordinate system, x,y,z, as shown in this figure describing the orientation of the internuclear vector **r** in the

principal axis system of the chemical shift tensor. The azimuthal angle alpha is the angle between the x axis (= d11) and the projection of the vector into the x,y plane (= d11, d22, "equatorial plane"). The polar angle beta is the angle between the vector and the z axis (= d33, "pole"). The polar angles are closely related to the type of Euler angles (p. 93) used by WSolids1. Because the dipolar interaction is axially symmetric, the two polar angles are sufficient to describe the relative orientations of chemical shift and dipolar interaction. For more general cases, the set of three Euler angles is required.

4.10 Euler Angles

The triplet of Euler angles (α, β, γ) is useful to describe rotations or relative orientations of orthogonal coordinate systems. Unfortunately, their definition is not unique and in the literature there are as many different conventions as authors. The convention employed here is one of the more common ones. All rotations are in a counter-clockwise fashion (right-handed, mathematically positive sense).



The Euler angles (α, β, γ) relate two orthogonal coordinate systems having a common origin. The transition from one coordinate system to the other is achieved by a series of two-dimensional rotations. The rotations are performed about coordinate system axes generated by the previous rotation step (the **step-by-step procedure** is illustrated in the topic Rotation Matrices (p. 94). The convention used here is that α is a rotation about the Z axis of the initial coordinate system. About the y' axis of this newly generated coordinate system a rotation by β is performed, followed by a rotation by γ about the new z axis.

Given the Euler angles, the step-by-step procedure illustrates how to move from one coordinate system to the other. However, given the two coordinate systems, how can one determine the Euler angles relating them? This is described in topic Determining Euler Angles (p. 95).

The usual ranges for α, β, γ are:

$$0 \leq \alpha \leq 360$$
$$0 \leq \beta \leq 180$$
$$0 \leq \gamma \leq 360$$

References

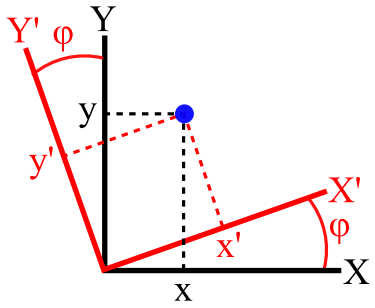
(1) G. Arfken, *Mathematical Methods for Physicists*, 3rd. ed., Academic Press: New York 1985.

(2) M. E. Rose, *Elementary Theory of Angular Momentum*, Wiley: New York 1957.

(3) K. Schmidt-Rohr and H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press: London 1994.

4.10.1 Rotation Matrices

Rotations or transformations from one coordinate system into another are conveniently described by the triplet of Euler angles (p. 93) (α, β, γ). Using the Euler angles, this three-dimensional problem can be dissected into a sequence of two-dimensional rotations, whereby in each rotation one axis remains invariant. Here, all rotations are counter clockwise (right-handed, mathematically positive sense).



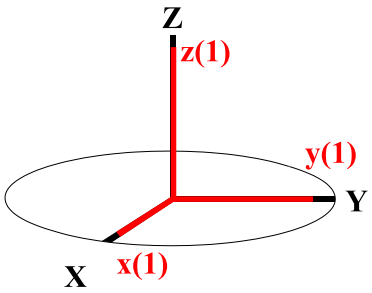
2D Analogy:
In order to simplify the problem, let us start with a two-dimensional rotation:
Suppose the coordinates, (x,y), of a point in the two-dimensional XY system are known, but we are actually interested in knowing the coordinates of this point in another coordinate system, X'Y', which is related to the XY system by a counter-clockwise rotation by an angle φ.
As the figure indicates, the coordinates of the given point in the new coordinate system will be:

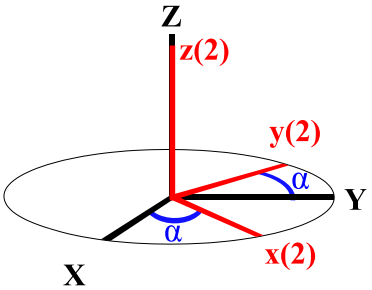
$$\begin{aligned} x' &= x\cos\varphi + y\sin\varphi \\ y' &= -x\sin\varphi + y\cos\varphi \end{aligned}$$

or, in matrix notation:

$$R(\varphi) = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}$$

Start: Coincidence
Now, transferred to a three-dimensional problem, the goal will be to describe the coordinates in a final rotated system (x,y,z) which is related to some initial coordinate system (X,Y,Z) by the Euler angles. The final system is developed in three steps, each step involving a rotation described by one Euler angle. At the start, both coordinate systems, (X,Y,Z) and (x(1), y(1), z(1)), shall be coincident.

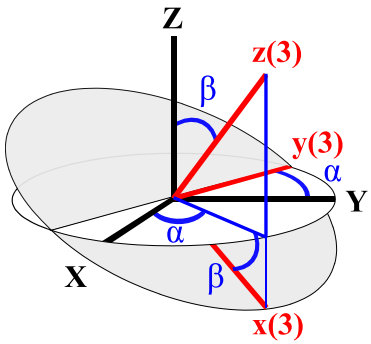




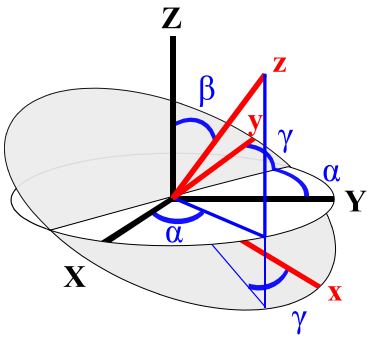
First Rotation:
The first rotation involves the Euler angle α. The x(1), y(1), z(1) axis system is rotated about the Z axis through an angle α counterclockwise relative to X,Y,Z to give the new system x(2), y(2), z(2). It is clear from the figure that this rotation mixes the coordinates along X and Y, completely analogous to the two-dimensional rotation described above, while the coordinate along Z remains unaffected. The rotation matrix to describe this operation is given by:

$$R_z(\alpha) = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Second Rotation:
The second rotation involves the Euler angle β. The x(2), y(2), z(2) axis system is rotated about the y(2) axis through an angle β counterclockwise to generate the new coordinate system x(3), y(3), z(3). Analogously to the first Euler rotation, this mixes the coordinates along x(2) and z(2), while the coordinate along y(2) remains unaffected. This operation also generates a line of nodes parallel to the direction of y(2). The rotation matrix to describe this operation is given by:



$$R_y(\beta) = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix}$$



Third Rotation:
The last rotation involves the Euler angle γ. The x(3), y(3), z(3) axis system is rotated about the z(3) axis through an angle γ counterclockwise to generate the final coordinate system x, y, z. Analogously to the first Euler rotation, this mixes the coordinates along x(3) and y(3), while the coordinate along z(3) remains unaffected. The rotation matrix to describe this operation is given by:

$$R_z(\gamma) = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The combined effect of these three rotations is given by this transformation matrix:

$$R_z(\gamma)R_y(\beta)R_z(\alpha) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}$$

Note: This type of rotation about sequentially newly generated axes produces the same result as rotations by the same angles about the fixed original axes, if the order of angles is reversed: $R_Z(\alpha)R_Y(\beta)R_Z(\gamma)$ (cf. Mehring's book, appendix [1]).

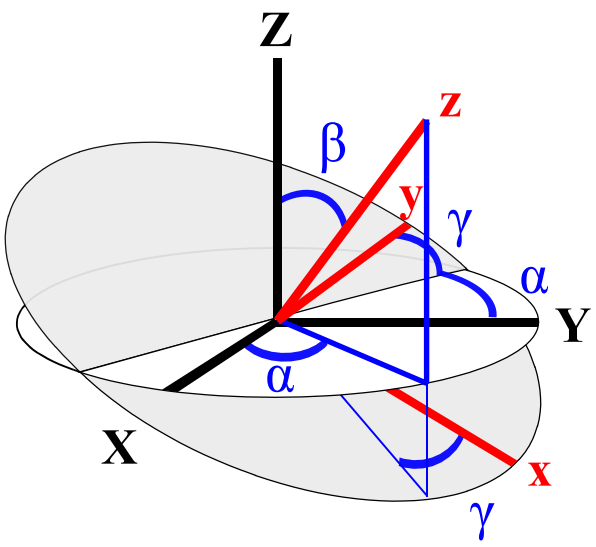
References

(1) M. Mehring, *Principles of High Resolution NMR in Solids*; 2nd ed.; Springer-Verlag, Berlin, 1983.

4.10.2 Determining Euler Angles

Given the relative orientations of two coordinate systems, how does one go about determining the Euler angles relating them?

First, one needs to decide which coordinate system to take as the **reference coordinate system**, **X,Y,Z**, and which one as **derived coordinate system**, **x,y,z**. Because the Euler transformations allow to switch between coordinate systems easily, it does not matter which one is selected.



The angle β is simply the angle between the z axes of both coordinate systems. The angle α is the angle between the X axis of the reference coordinate system and the projection of z into the X,Y plane. Finally, γ is the angle between the y axis and the line of nodes.

4.11 Electric Field Gradient Tensor

A quadrupolar nucleus S, with nuclear spin S $> 1/2$, is subject to an interaction of the nuclear quadrupole moment, $e\mathbf{Q}$, with the component of the electric field gradient (EFG) along a particular direction, $V_{ii} = eq_{ii}$. The Laplace equation requires that the trace of the EFG tensor is zero. In addition, the EFG tensor is symmetric, hence consists only of 5 independent components. In its principal axis system (PAS), XYZ, the EFG tensor is diagonal and can be characterized by the three principal components V_{XX}, V_{YY}, V_{ZZ}. In nuclear quadrupole resonance (NQR), the principal components are labelled according to this convention:

$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$

Because of the trace of zero, only two independent parameters are required to characterize the magnitudes of the principal components, and these are usually chosen to be V_{ZZ} and the dimensionless asymmetry parameter η. The product of V_{ZZ} and the nuclear quadrupole moment is known as the quadrupolar coupling constant, χ:

$$\begin{aligned} \chi &= \frac{eV_{ZZ}Q}{h} = \frac{e^2q_{ZZ}Q}{h} \\ \eta &= (V_{XX} - V_{YY})/V_{ZZ} \end{aligned}$$

Thus, η is constrained to values between 0 and 1. The quadrupolar coupling constant should not be mixed up with the quadrupolar frequency, observed in NQR experiments.

4.12 Central Transition (CT) and Satellite Transitions (ST)

For a quadrupolar nucleus, with a nuclear spin greater than 1/2, as observed nucleus, one can select calculation of the central transition, 1/2 ↔ -1/2, spectrum only (CT), of the satellite transition, $m \leftrightarrow m - 1$ with $m \neq 1/2$, spectrum only (ST), or of all transitions.

CT	ST	Action

☑	☑	Calculates the total spectrum consistin of central transition and satellite transitions.
☑	☐	Calculates spectrum only including the central transition. Note that quadrupolar nuclei of integral spin don't have a central transition!
☐	☑	Calculates spectrum only including the satellite transitions.
☐	☐	This wouldn't calculate anything, therefore the default action is to calculate the central transition.

4.13 Variable-Angle Spinning Angle

The VAS angle specifies the angle between the direction of the external static magnetic field and the spinning axis.

4.14 Spinning Frequency

The spinning frequency is required in Hz. Although the sense of rotation does not affect the spectrum, valid values are limited to postive numbers. WSolids1 allows to have different spinning frequencies for different sites, although this doesn't make sense physically. This design flaw has been remedied in WSolids2.

4.15 Speedy Calculation

Some calculations are quite time consuming. In such cases, it is possible to select **Speedy calculation**, in which case only 1/16 of the orientations will be included. This is usually sufficient to reproduce the gross features of the line shape, but this gain in speed is bought at the expense of accuracy. In any case, a final calculation with Speedy Calculation disabled should be performed to verify the parameters.

4.16 INI File Settings

There are some settings in the WSolids1 INI file that might be of interest to the user. However, please make sure that you know what you are doing! From WSolids1 version 1.21 onwards, you can use the Settings (p. 40) dialog to change some of them temporarily or permanently.

The WSolids1 program will use one or two INI files to determine some default settings. There will always be one INI file in the same subdirectory as the executable, the master INI file. For non-portable versions of WSolids1 there will also be an INI file in the user's `My Documents` subdirectory. For more detailed information, see the next section.

4.16.1 Portable or Non-Portable Format: portable

```
[DOCUMENTS]
portable=1
```

There is one entry that will be checked at every start of WSolids1 : the value of `portable` in the `Document` section. If `portable` is set to 1, WSolids1 will consider itself as portable version and peruses the master INI file for all other default settings.

If `portable` equals 0, WSolids1 expects per user settings and from now on peruses the INI file in the user's documents directory (sub-directory `WSolids`). If this file does not exist yet because the current user has not started WSolids1 previously, the master INI file will be copied to this location.

I.e., changing the portability parameter in the master INI file makes WSolids1 portable or non-portable.

4.16.2 Default Output File Format: OutFile

```
[FILES]
OutFile=1
```

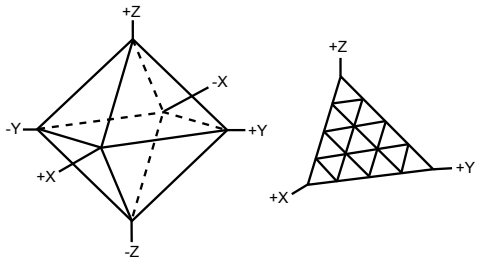
The parameter OutFile in the FILES section of the INI file preselects the standard output format of spectra. Currently, the value of OutFile, an integer, will correspond to the following file formats (see Save Spectrum (p. 22) for details):

OutFile	Format
1	WinNMR
2	Topspin
3	Solids
4	ASCII file
5	JCAMP-DX format

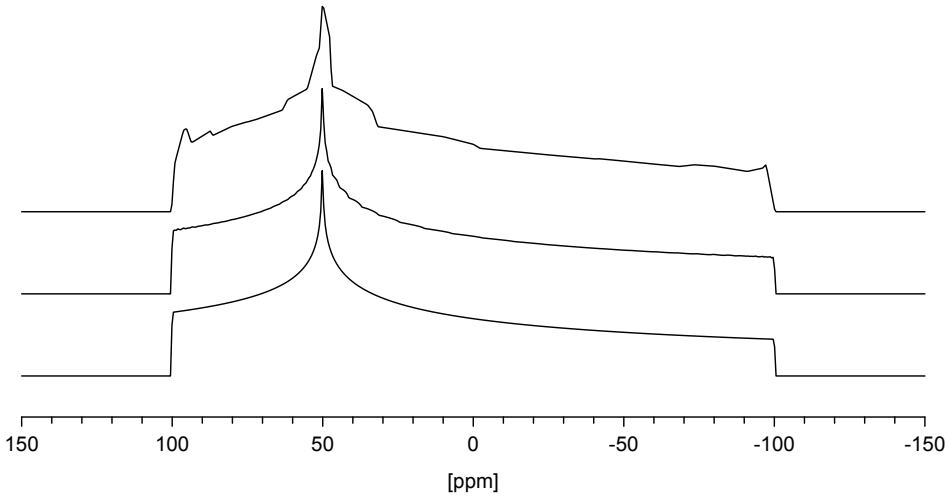
4.16.3 Number of Triangular Intersections (POWDER): NT

```
[Document]
NT=32
```

The parameter NT in the DOCUMENT section of the INI file determines the number of triangular intersections on the face of an octahedron, shown in the figure below for NT = 4. In the POWDER algorithm by Alderman, Solum and Grant, the frequencies and intensities are calculated at triangular intersections. For a given value of NT, there are $2NT^2 + 1$ different orientations. Usually, NT = 32 is a good compromise between speed of calculation and accuracy.



The figure below illustrates the effect of changing NT from 8 (top) to 32 (middle) to 256 (bottom). Note that for NT = 32 there are small ripples at the low-frequency side of δ_{22} and also close to δ_{11} and δ_{33}, while the spectrum for NT = 256 is very smooth.



D. W. Alderman, M. S. Solum, D. M. Grant, *J. Chem. Phys.* **1986**, *84*, 3717, DOI: 10.1063/1.450211.

4.16.4 Number of Decimal Digits: digits

```
[Document]
Digits=5
```

In order to fine tune the number of digits displayed in dialog boxes for floating point numbers, you can use the parameter `Digits` in the `DOCUMENT` section of the INI file. Note that `Digits` only affects the display, not the actual number of decimal digits evaluated when entering floating point numbers. I.e., the accuracy is not affected by `Digits`!

5 Acknowledgements

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5.1 Credits

- Some of the early FORTRAN modules were written by:
  William P. Power (dipolar-chemical shift NMR, quadrupolar powder patterns QUADPOW and SECQUAD)
  Gang Wu (dipolar-chemical shift NMR of homonuclear spin pairs)
- This program contains for space-tiling and interpolation purposes the POWDER routine. We are grateful to **D. W. Alderman** for a copy of the routine in FORTRAN.
  D. W. Alderman; M. S. Solum; D. M. Grant; *J. Chem. Phys.* **1986**, *84*, 3717, DOI: 10.1063/1.450211.
- **Dr. Alejandro C. Olivieri** kindly provided BASIC programs that taught me how to calculate spinning sidebands in the frequency domain:
  Olivieri, A. C. *Solid State Nucl. Magn. Reson.* **1997**, *10*, 19-24,
  DOI: 10.1016/S0926-2040(97)00023-4;
  Olivieri, A. C. *Solid State Nucl. Magn. Reson.* **1998**, *11*, 181-187,
  DOI: 10.1016/S0926-2040(98)00035-6;
- We learned a lot from **A. C. Olivieri**'s BASIC program ANYCHI to calculate the MAS spectrum of a spin-1/2 nucleus coupled to a spin-3/2 nucleus:
  S. H. Alarcon; A. C. Olivieri; R. K. Harris; *Solid State Nucl. Magn. Reson.* **1993**, *2*, 325.
  We are grateful to Alejandro C. Olivieri for making his program available.
- The design of WSolids1 received some ideas gained by working with the program ANTIOPE. We are grateful to **John S. Waugh** for making a copy of this program available to us:
  F. S. de Bouregas; J. S. Waugh; *J. Magn. Reson.* **1992**, *96*, 280.
- Thanks are due to **Jim Frye** and **Glenn Sullivan**, both Chemagnetics/Varian NMR, for their help with the implementation of the SpinSight file import.
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- We acknowledge the notes by **W. M. Westler** and **F. Abildgaard** posted on the internet on DMX Digital Filters and Non-Bruker Offline Processing
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W. H. Press, S.A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in C*, Cambridge University Press: Cambridge 1992.

- Microsoft for providing `Visual C++ 2008 Express Edition` for free
- **Jordan Russell** for making `Inno Setup` available (`http://www.jrsoftware.org/`)
- **Jochen Kalmbach** for demonstrating how to statically link against the Microsoft CRT and thus get rid of `VCREDIST_X86.EXE` (`http://blog.kalmbach-software.de`)
- "**chicks**" for demonstrating in his `pdfp` PDF tools how to establish Dynamic Data Exchange (DDE) with Adobe Acrobat (Reader) (`http://www.esnips.com/web/PDFTools`)
- This manual has been produced using the MiKTEX (`http://www.miktex.org`) distribution of LATEX in combination with the TeXstudio editor (`http://texstudio.sourceforge.net/`), or TeXnicCenter editor (`http://www.ToolsCenter.org`) initially.
- **Irfan Skiljan**'s `IrfanView` (`http://www.irfanview.com/`) has been used to process bitmapped images, and `Inkscape` (`www.inkscape.org`) for dealing with vector graphics.
- The routines for complex matrix inversion are based on the code examples by PMD from MIT, shown for the Santa Barbara Channel Experiment (SBCX).
- My prefered PDF viewer is the free PDF XChange Editor (by Tracker Software Products, Ltd., `http://www.tracker-software.com`), more powerful and reliable than the Adobe Acrobat Reader.
- Thanks to **Guy Bernard** (University of Alberta) for pointing out a bug in my jcamp input.
- I am grateful to **Kirk Marat** (University of Manitoba) for his help making the JCAMP-DX files produced by WSolids1 palatable to SpinWorks.

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